INSTITUTE OF HYDROLOGY

NUTRIENT CYCLING IN THE WYE AND SEVERN AT PLYNLIMON

by

G ROBERTS, J A HUDSON and
J R BLACKIE

ABSTRACT

This report describes the results obtained in a study, funded by the Ministry of Agriculture, Fisheries & Food, into nutrient (nitrogen, phosphorus and potassium) concentrations in streams draining rough pasture and established forestry at Plynlimon, mid-Wales. Nutrient losses from each of the land uses are calculated and related to input in rainfall. The results show a marked seasonal variation in nitrate-N concentrations in the streams draining both land uses and higher nitrate-N concentrations in the stream draining the forested catchment during and following the drought year 1976. These phenomena are explained in terms of the growth and decay cycle of plants and the different responses to drought of grassland and forest respectively. Nutrient balances show a net input of 10 kg/ha annually of nitrogen and parity for potassium and phosphorus for each of the land uses.

REPORT NO 86

July 1983

CONTENTS

		Page
1	INTRODUCTION	1
2	LOCATION OF STUDY AND DATA COLLECTION	2
3	RESULTS OF THE MONITORING EXERCISE	6
3.1	Nutrient concentrations in runoff and rainfall	6
3.2	Nutrient loadings in rainfall and runoff	15
3.3	Nutrient balances for the Wye and Severn catchments	15
3.4	Upland stream concentrations in the wider drainage basin context	24
4	FURTHER ANALYTICAL OBJECTIVES	26
4.1	Suggested explanations of the general patterns in stream nutrient concentrations	26
	General trend in nutrient losses from upland catchments	26
	Within catchment variation in nutrient losses	31
	Modifying influences to the general patterns of stream nutrient losses	41
4.2	Comparative nutrient budgets for the Wye and Severn catchments	46
	Extreme events	46
	Are the differences between the two catchments significant when compared to the within-catchment variations in nutrient levels	46
	The implications for water quality of land use change to forestry	48
5	CONCLUSIONS	49
6	DISCUSSION	50
6.1	Review of present study	50
	Data collection techniques	51
	Required supplementary data	52
6.2	Nutrient cycling in upland Britain	53
	Review of past and present studies	53
	Future work	54
	REFERENCES	55

1 INTRODUCTION

Disputes between agriculture and forestry have been a feature of upland land use planning since the Forestry Commission initiated systematic planting of coniferous trees, mainly for strategic purposes, after the 1914-18 war, but they have rarely reached the intensity of the present time. Technological revolutions in agriculture have shifted the emphasis to the extent that areas once thought of as only suitable for rough grazing or forestry now have the potential to contribute towards self sufficiency in food production. The development of previously underexploited areas, such as the mid-Wales uplands, will almost certainly be central to the conflict.

The controversy has acted as a catalyst for intensive scientific research in the uplands, not only into agricultural and forestry technology but also into the secondary or side effects of land use change, ie. conservation, recreation, social considerations and, perhaps most importantly, changes in quantity and quality of water resources. Until now decisions of land use policy have relied on political, strategic and economic arguments with good husbandry and environmental considerations not a little way behind. The cynic's view is that the arguments are subjective and heavily biased by self interest and not, as should be the case, by the need to treat the spectrum of upland productivity as a resource vital to Britain's future well-being.

As a clue to the future of land-use changes, recent work on plant breeding and potential pasture production (Munro *et al*, 1973) has shown that by changing the composition of the grass sward together with regular applications of fertilizer, nitrogen in particular, yields and hence stocking rates in uplands can be dramatically increased. Similarly, forestry practice recommends applications of nitrogen, phosphorus and potassium (NPK) fertilizer during establishment followed by regular P applications to stimulate growth. If the intention of the Forestry Commission to afforest 2½ million hectares in upland Britain before the end of the century (Forestry Commission, 1977) comes to fruition at the same time as an explosion in agricultural production, the uplands of Britain could become a patchwork of sources for potential pollutants, mainly in the form of runoff of fertilizer nutrients.

The water authorities have a statutory obligation to monitor the concentrations of solutes in water courses to check mainly for point sources of industrial and agricultural pollutants. Because there has been no obvious pollution problems associated with upland areas, their effort has been concentrated in the lower reaches of the river systems and changes in water quality in upland streams caused by land use practices have not been monitored extensively.

The water quality effects of upland pasture improvement and of various phases of afforestation are currently the subject of collaborative research between the Institute of Hydrology and the Agricultural Development Advisory Service, the Forestry Commission and the Water Research Centre. However, before changes in water quality resulting from these management operations can be assessed it is necessary to quantify and explain the present (background) levels of nutrients in forested and non-forested streams. Therefore, in parallel with a long-term study of the differences in water usage of established coniferous forest and rough pasture, the Institute has been monitoring the nutrient loadings of streams draining catchments under these two important upland land uses.

The dependence of water quality on the nature of water movement through a catchment is well appreciated and though levels of N, P and K in upland streams are, at present, of little significance to water resource management (N, P, K, are limiting to micro-organism growth and do not, as yet, affect potability), an explanation of background levels as a function of nutrient availability and hydrological response is a major step towards identification of pollutant pathways and predictions of future nutrient levels.

In an area that is typical of potential reservoir catchments the welding together of information of this kind is crucial to sensitive land use planning. This study is intended to provide a background comparison between nutrient levels from forested and grassland catchments that goes hand in hand with other comparisons carried out by the Institute on the subject of comparative water balances (IH Report No. 33, 1976) and of sediment yields from forest and grassland (Painter *et al*, 1974).

2 LOCATION OF STUDY AND DATA COLLECTION

The study was carried out on two experimental catchments in the Plynlimon range of hills in mid-Wales where the Institute of Hydrology have also been conducting a study of the hydrological characteristics of established forestry and of rough pasture (IH Report No. 33, 1976). The two catchments are fully instrumented to measure rainfall, runoff and evaporation (see Fig. 1), and complete data since 1971 are available. The altitude range in the two catchments is 320-740 m and the mean annual rainfall is 2500 mm.

One catchment, the Wye, is 1055 ha in area and is composed of 62% acid grassland, 10% heath, and 28% mire vegetation. In terms of soil/vegetation associations these proportions are typical of large areas of upland Wales corresponding to agricultural potentials of U3S and H2 to H4 on the MAFF (ADAS) Hills and Upland Classification (Fig. 2). The main soil types are peats, peaty podsols, acid brown-earths, and peaty gleys. Chemical analyses of soil samples showed a pH of 4.6 and total nitrogen content of 2.3% in the top 30 cm layer. The soils were also found to be deficient in phosphorus, potassium and magnesium. Some 25% of the area has been subjected to various forms of improvement mainly in the 1920s and 1930s. Fertilizer in the form of basic slag is spread on a small percentage of the catchment every two or three years.

The other catchment, the Severn, is 870 ha in area and, in terms of its soils/vegetation associations, was similar to the Wye prior to the afforestation of 70% of its area over a period of 25 years beginning in 1937; the remaining 30% is composed of peaty bogs and rocky outcrops. An aerial application of mineral phosphate and potassium was made to the forested areas in the autumn of 1974. A detailed description of the vegetation and physiography of the Plynlimon catchments is given by Newson (1976).

Water sample collection at the outfalls of the Wye and Severn began in July 1976 and was continued until July 1980. Originally, two automatic liquid samplers were employed in each stream, one collecting a sample every eight hours and the other, triggered by rising stage, collecting a sample every 30 mins during high flow periods. This 'storm' sampling was discontinued in October 1977. The samples were stored in brown glass bottles and collected once a week. Studies of changes in

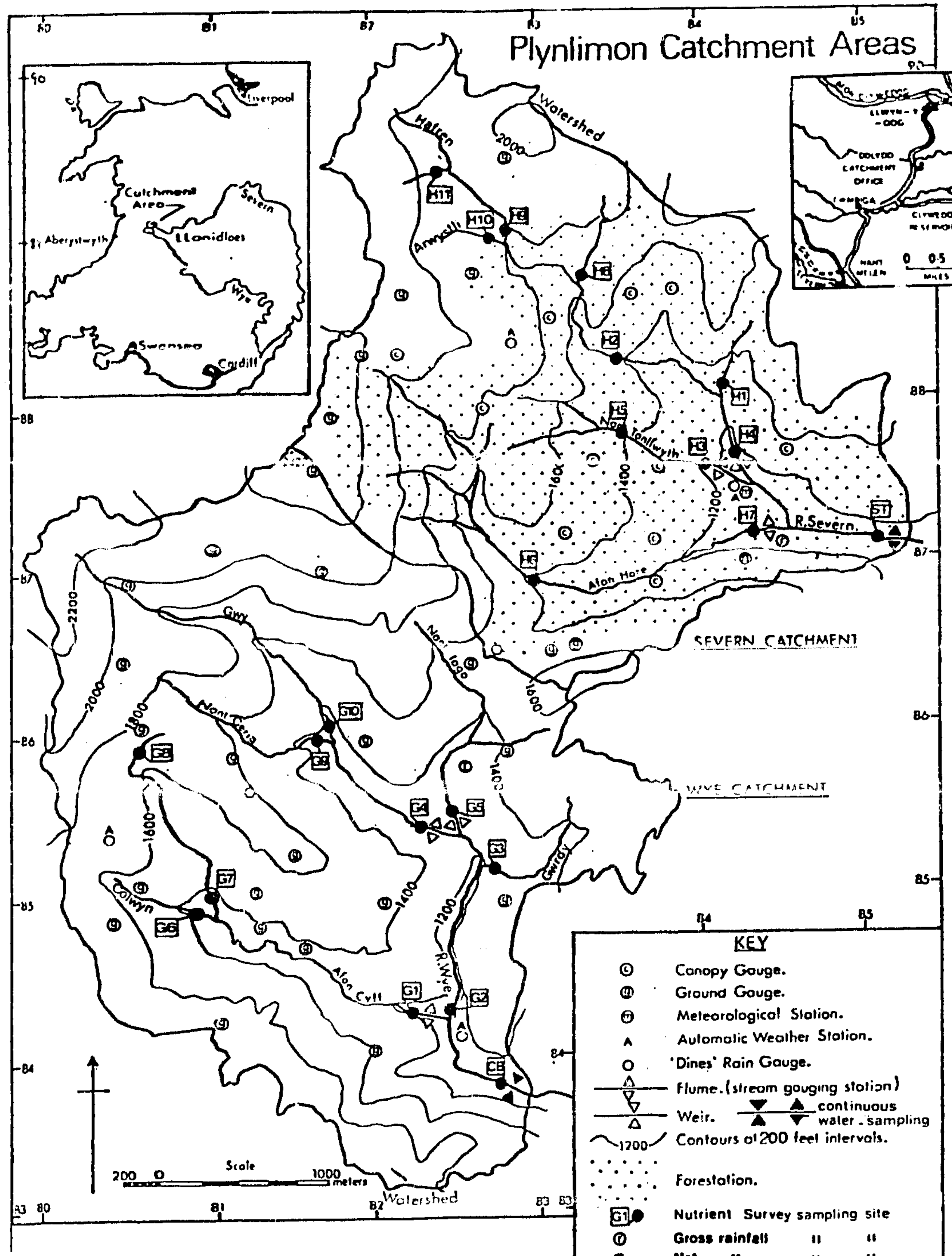


FIGURE 1 Water quantity and quality instrument networks

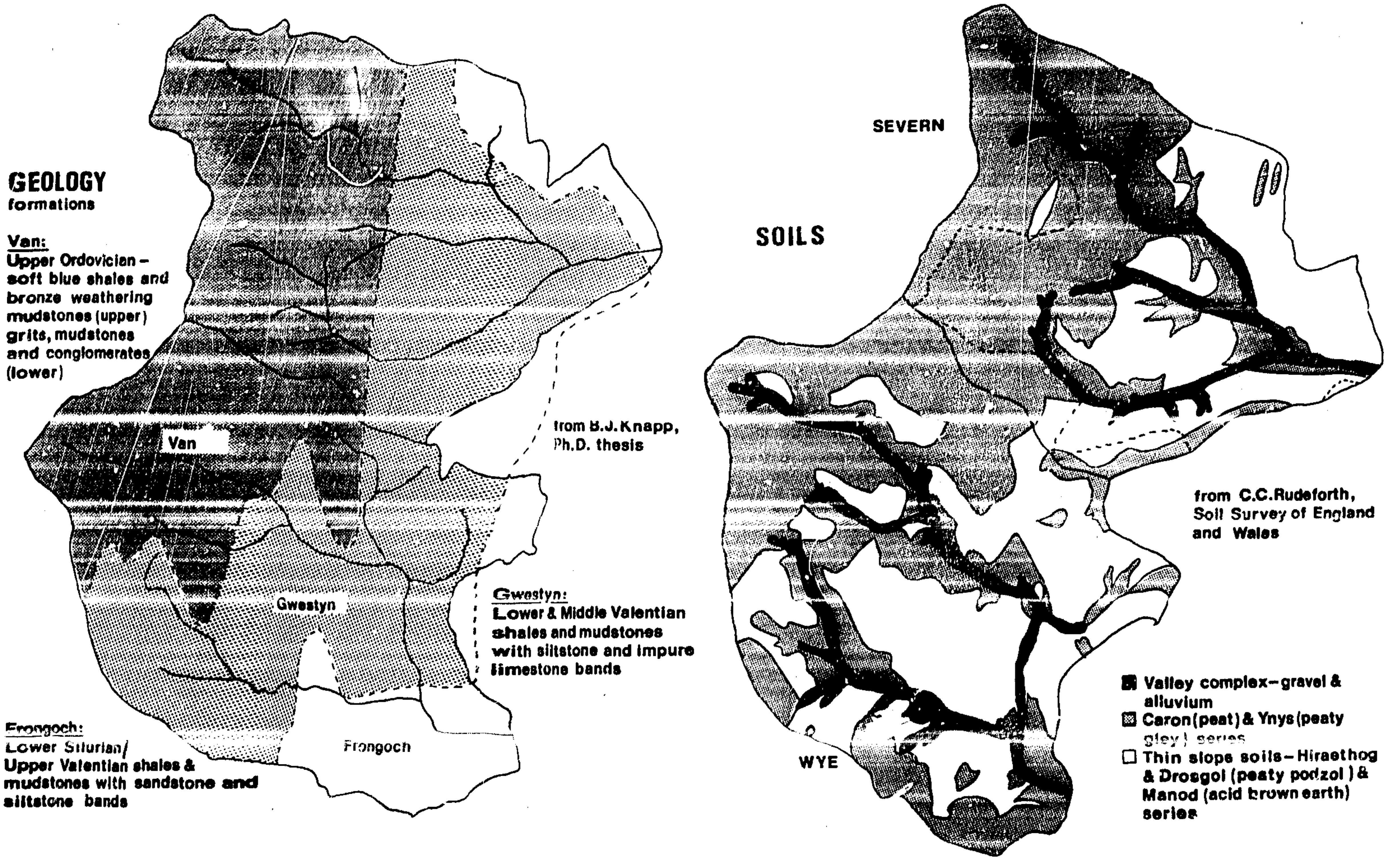


FIGURE 2 Plynlimon catchment characteristics

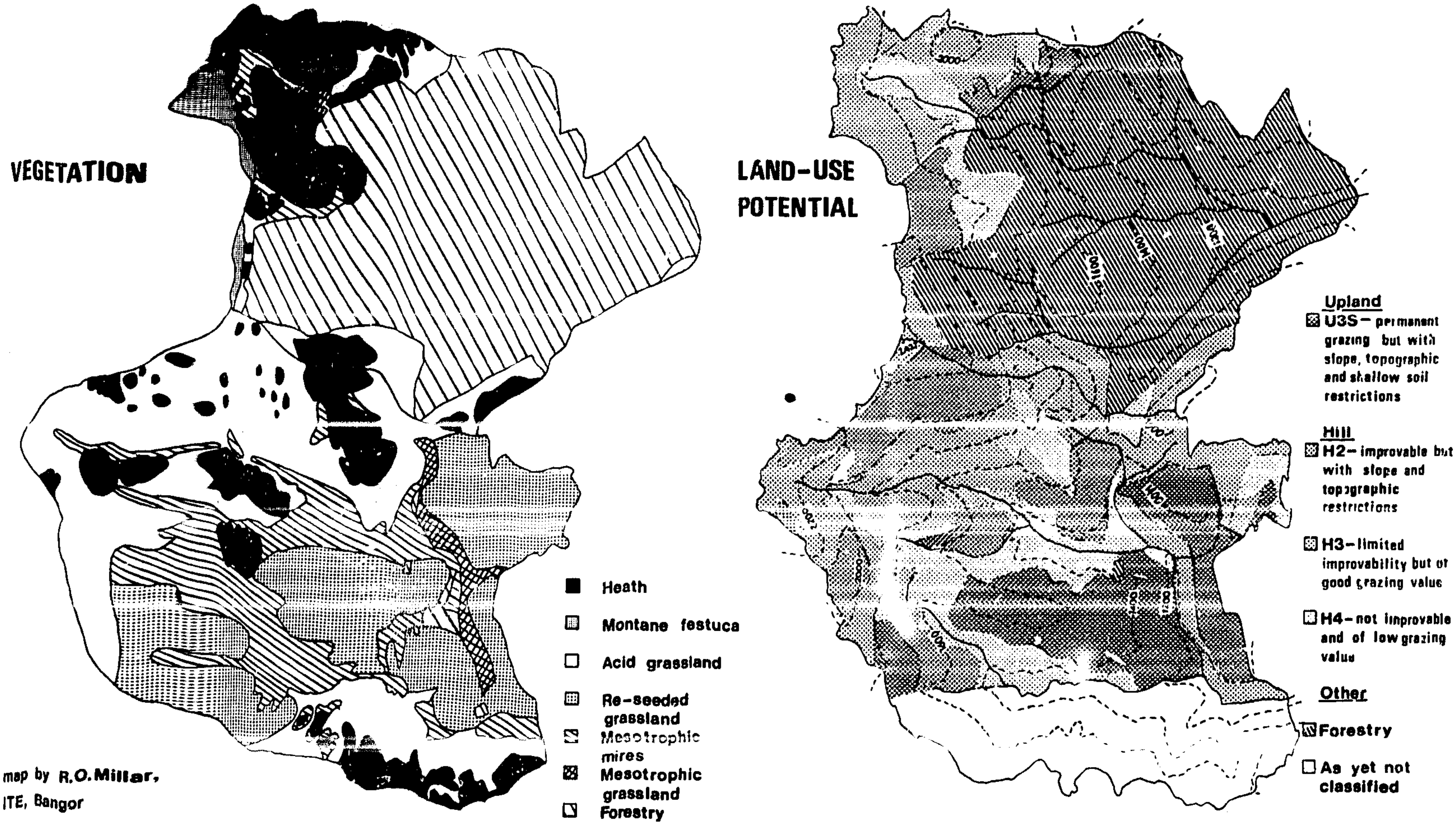


FIGURE 2 contd. Plynlimon catchment characteristics chemical composition over time indicated that it was unnecessary to preserve the samples chemically.

Rainfall sampling began in November 1977 in the Wye catchment and in December 1979 in the Severn catchment. These rainfall samples were collected using a Meteorological Office standard 1 ft raingauge, the sample being stored in a brown 1 litre glass bottle. The samples were collected at weekly intervals and if insufficient sample was obtained, then it was stored in a refrigerator and added to the sample from the following week. The samples were unfiltered, so the results of the chemical analyses can be regarded as referring to 'bulk precipitation' as defined by Whitehead and Feth (1964). No preservative was added to the samples because of the problems associated with maintaining a correct sample/preservative ratio.

All the samples were analysed at MAFF Trawscoed for ammonium-N, nitrate-N, total-N, phosphorus and potassium. The analyses were carried out according to recommendations in the Department of the Environment publication, "Analysis of Raw, Potable and Waste Waters" (HMSO, 1972). The inorganic forms of nitrogen were individually converted to ammonia and determined colorimetrically after the addition of Nessler's reagent. Total unoxidized nitrogen was extracted by the Kjeldahl method and determined colorimetrically as above. Total nitrogen and organic nitrogen were calculated as total unoxidized-N + nitrate-N and total unoxidized-N - ammonium-N respectively. Total inorganic phosphorus was determined colorimetrically as orthosphosphate after conversion to molybdenum blue and potassium was determined by flame photometry. The limit of detection of each of the chemical analyses was 0.02 mg/l. For a small part of the study, pH measurements were also taken.

Originally, each sample was analysed but to reduce the work load, it was decided to combine three of the eight hourly samples to produce a daily sample and two 30-min samples to produce an hourly sample. As a further reduction, the phosphorus and potassium analyses were limited to one per week in the case of the continuous sampling and to one per storm in the case of the 'storm' sampling.

3 RESULTS OF THE MONITORING EXERCISE

The most widely used index of water quality in natural waters is concentration, normally expressed in mg/l or parts per million (ppm). Nutrient concentrations control the rate of micro-organism growth and, at high levels, may be toxic, especially to young children. However, when calculating nutrient balances and predicting downstream nutrient concentrations in river reaches, reservoirs and lakes, resulting from multiple inputs of different quality, an equally important index of water quality is the product of concentration and flow or rain, normally termed the loading, expressed in kg/ha. For this reason, the results reported for flow and rain in the following sections are in terms of both concentration and loading.

3.1 Nutrient concentrations in runoff and rainfall

A time series presentation of the nutrient concentrations found in the discharges of the Wye and Severn is given in Fig. 3. The data are presented as weekly mean

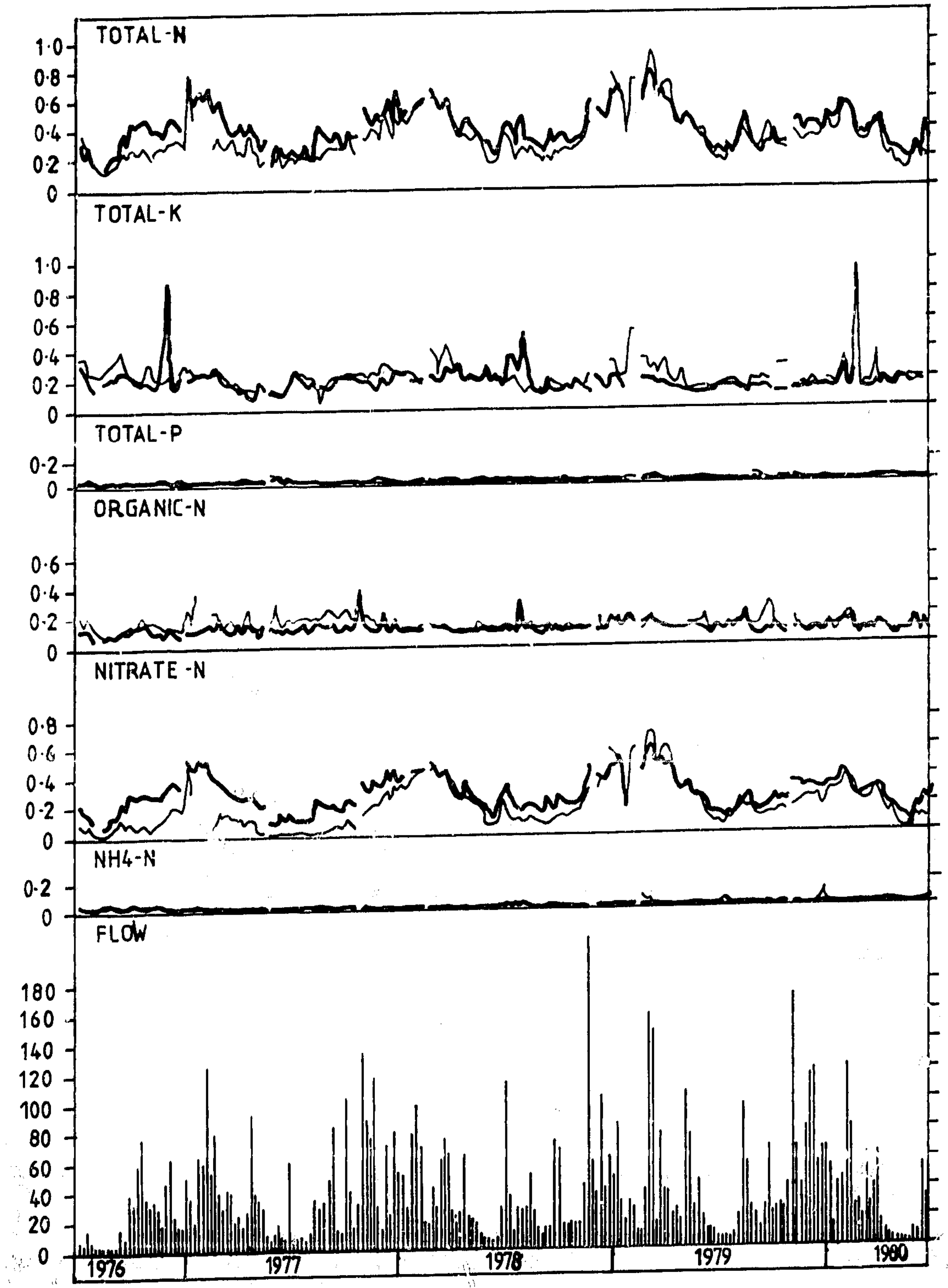


FIGURE 3 Nutrient concentrations and weekly flows in the Wye and Severn

Wye ——— Severn ━━━

concentrations (not flow weighted) as the best illustration of trends and variations; the average total weekly flows of the Wye and Severn are included for comparison. Gaps appear in the data caused mainly by instrument malfunction and/or freezing of sample bottles.

In comparison with the concentrations found in lowland reaches of major British rivers these values are much lower, often by an order of magnitude, and reflect the generally low agricultural activity and the lack of industrial or domestic effluent input to the river systems in the uplands. The concentrations were in the following ranges:-

Total N	0→1.6 mg/l
Total P	0→0.1 mg/l
Total K	0→0.9 mg/l
Ammonium-N	0→0.2 mg/l
Nitrate-N	0→0.8 mg/l
Organic-N	0→1.3 mg/l

The concentrations were sometimes below the limit of detection of the analyses used (0.02 mg/l); in such cases a value of 0.01 mg/l was substituted. Such limits may be adequate for N and K but are only suitable for an order of magnitude study of P and far too crude for a sensible speculation on causes of phosphorus concentration variation or the calculation of phosphorus balances in the Wye and Severn catchments.

A summary of annual mean concentrations (not flow weighted) for the two catchments over the four year study period is given in Table 1. The choice of July to June as the annual cycle was dictated by the start and end dates of the study.

The most interesting variation in nutrient concentration is shown by nitrate-N which exhibits a seasonal distribution, not quite sinusoidal, with a marked winter peak. Similar trends were found by Read *et al.* (1981) in their study in northeast Scotland and by Hill (1978) during his study of several drainage basins in Toronto. In general, the rising limb of the wave has a gentler slope culminating in peak concentrations in January 1977, March 1978, March 1979, and January 1980, followed by a more rapid decline through each spring period. The skewed position of the peak is crucial to the explanation of the variation in nitrate-N concentration and this is discussed further in section 4. Also, the nitrate-N concentrations in the discharge of the Severn are higher than in the discharge of the Wye particularly during 1976 and 1977. The significance of this in terms of nutrient cycling in forested and grassland areas is discussed in section 4. Ammonium-N concentrations on the other hand, exhibit little seasonal variation and are similar in the discharges of the two catchments. There is evidence, however, of slightly higher mean ammonium-N concentrations in the drought years 1976/77 than in subsequent years caused, in all probability, by the higher concentrations of ammonium-N in rainfall during dry periods. Total N concentrations reflect the seasonal variation and catchment differences exhibited by nitrate-N concentrations superimposed by sharp, high concentration peaks. These peaks are attributed to changes in the concentrations of organic N and generally occur during periods of high flow particularly following long dry periods. The organic N concentrations in the Wye tend to respond more to the general autumn increase in base flow than those in the Severn; this is particularly noticeable in 1976 and 1977. This may be caused by desiccation erosion, particularly of peat. The fact that the magnitude of response to increasing flow is greatest in the Wye supports this hypothesis, as the Severn showed less evidence of desiccation than the Wye in 1976.

TABLE 1 MEAN ANNUAL NUTRIENT CONCENTRATIONS AND LOADINGS FROM THE WYE AND SEVERN

MEAN ANNUAL NUTRIENT CONCENTRATIONS, mg/l (not flow weighted)

	WYE								SEVERN							
YEAR	RAIN	FLOW	NH_4^+N	NO_3^-N	SOLUBLE ORGANIC N	TOTAL N	P	K	RAIN	FLOW	NH_4^+N	NO_3^-N	SOLUBLE ORGANIC N	TOTAL N	P	K
7/76-6/77	2074	1649	0.02	0.10	0.14	0.26	0.02	0.22	2094	1364	0.02	0.26	0.11	0.39	0.01	0.19
7/77-6/78	2459	2123	0.01	0.17	0.16	0.34	0.02	0.23	2555	1968	0.01	0.28	0.13	0.42	0.01	0.21
7/78-6/79	2555	2370	0.01	0.28	0.13	0.42	0.01	0.19	2542	2123	0.01	0.31	0.12	0.44	0.02	0.16
7/79-6/80	2623	2218	0.01	0.18	0.12	0.32	0.01	0.20	2577	1970	0.01	0.24	0.10	0.35	0.01	0.16

NUTRIENT LOSSES kg/ha

	WYE								SEVERN							
YEAR	RAIN	FLOW	NH_4^+N	NO_3^-N	SOLUBLE ORGANIC N	TOTAL	P	K	RAIN	FLOW	NH_4^+N	NO_3^-N	SOLUBLE ORGANIC N	TOTAL N	P	K
7/76-6/77	2074	1649	0.31	2.26	2.81	5.38	0.27	3.60	2094	1364	0.23	4.68	1.71	6.62	0.19	2.83
7/77-6/78	2459	2123	0.25	5.15	3.51	8.91	0.33	5.13	2555	1968	0.21	6.61	2.71	9.53	0.34	3.90
7/78-6/79	2555	2370	0.35	8.46	3.24	12.05	0.34	5.06	2542	2123	0.23	8.38	2.78	11.39	0.33	3.61
7/79-6/80	2623	2218	0.30	4.83	2.72	7.85	0.25	4.28	2577	1970	0.23	5.90	2.33	8.46	0.26	2.87

There are slight indications that phosphorus concentrations in the discharge of the Wye catchment were greater in 1976-78 than in 1978-80. This again may be caused by desiccation and erosion of organic materials and sediment following the drought year 1976. The lack of a similar trend in phosphorus concentrations in the discharge of the Severn catchment (where the highest average concentration occurred in 1978/79) may again be a reflection of the smaller amount of desiccation in the Severn.

Mean annual potassium concentrations show a small but significant drop over the study period in both catchments, especially the Severn. There is some evidence of seasonal variation in potassium concentrations with a summer minimum and an autumn or winter maximum. In general, the potassium concentrations in the Wye are higher than those in the Severn, though, for certain periods, notably July and August 1978, the reverse is true. An analysis of the relationship between concentration and other hydrological variables is difficult for potassium because from December 1976, samples were bulked to give weekly mean concentrations. Data from the first six months of the study, however, do show some correlation with flow especially in September 1976 during which potassium concentrations in both streams responded to an increase in flow after the long dry period (Fig. 4); subsequent peaks in flow, though higher, did not produce the same effect thus confirming the early autumn runoff as the major flushing agent (Walling and Foster, 1975). It is also interesting to note the different response of the Wye and the Severn to minor flow peaks in late autumn. An increase in flow in early November 1976 produced a massive rise in the Severn and a small rise in the Wye. This suggests that they are caused by isolated occurrences of soil erosion arising from bank collapse or gully washout.

The results of the chemical analyses carried out on the rainfall samples are shown in Fig. 5 together with the mean weekly rainfall totals.

The range of nutrient concentrations in the rainfall samples, shown below, is much greater than in the runoff.

Total N	0→8.0 mg/l
Total P	0→0.1 mg/l
Total K	0→2.5 mg/l
Ammonium-N	0→6.9 mg/l
Nitrate-N	0→2.4 mg/l
Organic-N	0→1.8 mg/l

For determining nutrient inputs to the catchments it is assumed that the one rainfall sampling site, situated in the Wye catchment, is representative in quality, if not in quantity, of both catchments. Although there must be some spatial variation in rainfall quality over such a large area, there are no obvious sources of industrial pollution capable of causing large spatial nutrient gradients in the atmosphere. A comparison of the nitrogen concentrations in the Severn catchment during the same periods in 1980 (Table 2 and Fig. 6) shows that the general trends are similar but that for certain periods, notably 19.6.80-26.6.80, very obvious differences emerge. This particular disparity is caused by a high concentration of soluble organic nitrogen in the Severn rainfall (1.02 mg/l) that is not mirrored in the Wye rainfall (0.15 mg/l) and is probably due to contamination by organic matter, possibly wind blow of pine needles from nearly trees. It is also obvious, however, that not all of the high values that are common in the summer months of the four years under study can be attributed to contamination and that the high nutrient concentrations in summer rainfall are in fact real (Ångström and Högberg, 1952, Eriksson, 1952): the highest total inorganic nitrogen concentration recorded in the

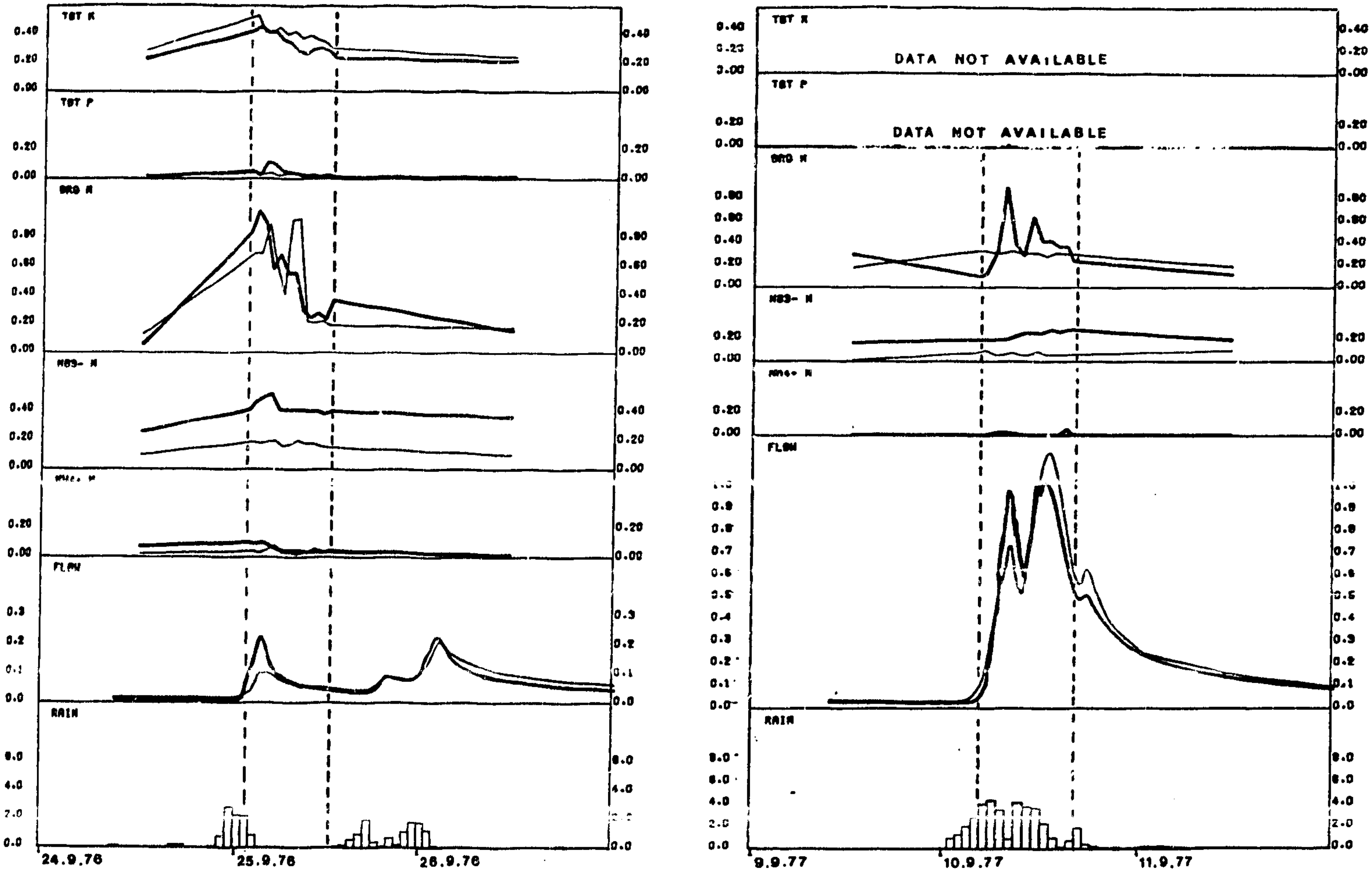


FIGURE 4 Nutrient concentrations during two storm events. Wye —— Severn ▬▬ Limit of storm sampling ┆ ┆

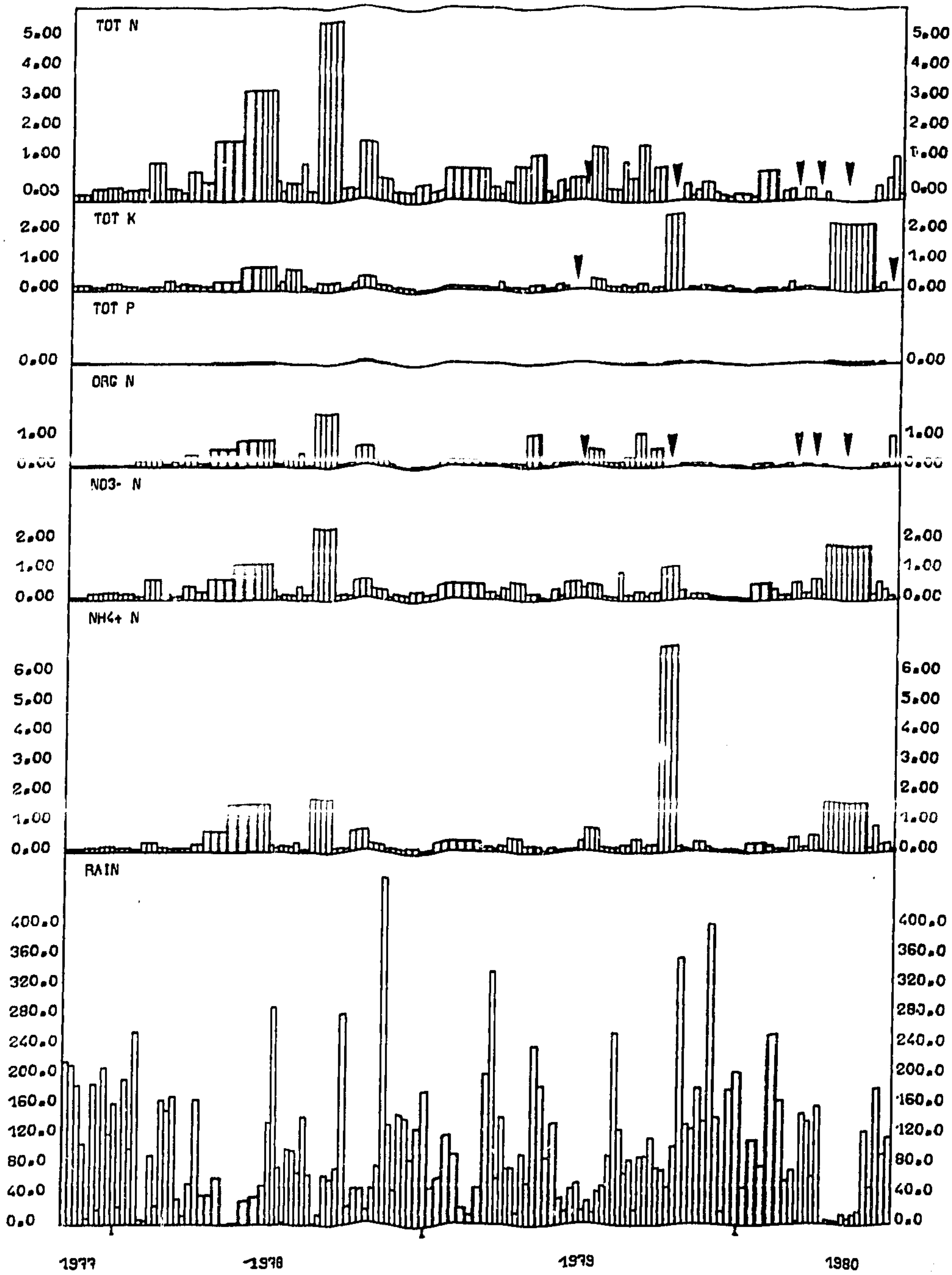


FIGURE 5 Nutrient concentrations (mg/l) in the rainfall RAIN (mm) in first graph

▼ INDICATES MISSING DATA

TABLE 2 NITROGEN CONCENTRATIONS AND INPUTS IN RAINFALL SAMPLES COLLECTED IN THE WYE AND SEVERN CATCHMENTS (TOTAL N CONCENTRATIONS ARE EXPRESSED AS > NH_4^+ N + NO_3^- N WHEN NO FIGURE OBTAINED FOR SOLUBLE ORGANIC N).

PERIOD ENDING	WYE CATCHMENT						SEVERN CATCHMENT					
	RAIN (mm)	CONCENTRATIONS (mg/L)				LOAD N (KG/HA)	RAIN (mm)	CONCENTRATIONS (mg/L)				LOAD N (KG/HA)
		NH_4^+ N	NO_3^- N	ORG.N	TOTAL N			NH_4^+ N	NO_3^- N	ORG.N	TOTAL N	
3.1.80	134.5	0.11	0.17	0.14	0.42	0.58	116.5	0.10	0.10	0.07	0.27	0.31
9.1.80	80.3	0.04	0.04	0.01	0.09	0.07	60.7	0.07	0.09	0.01	0.17	0.10
24.1.80	103.6	0.39	0.55	0.19	0.13	1.17	79.7	0.32	0.57	0.14	1.03	0.82
30.1.80	33.7	0.17	0.20	0.02	0.39	0.13	29.4	0.23	0.37	-	>0.60	-
7.2.80	144.3	0.10	0.15	0.17	0.42	0.61	151.6	0.11	0.16	0.06	0.33	0.50
15.2.80	67.1	0.05	0.09	0.05	0.19	0.13	75.7	0.09	0.16	0.13	0.38	0.29
28.2.80	42.7	0.69	0.59	0.13	0.41	0.60	56.3	0.48	0.55	-	>1.03	-
13.3.80	124.9	0.11	0.11	0.02	0.24	0.30	102.1	0.13	0.19	0.06	0.38	0.39
27.3.80	72.7	0.39	0.45	0.23	1.07	0.78	61.1	0.52	0.66	-	>1.18	-
2.4.80	73.3	0.11	0.15	-	>0.26	-	61.1	0.06	0.16	0.06	0.28	0.17
30.5.80	51.0	1.75	1.04	-	>2.79	-	42.5	1.67	1.81	-	>3.48	-
6.6.80	60.5	0.16	0.15	0.13	0.44	0.27	59.1	0.16	0.22	0.13	0.51	0.30
12.6.80	20.7	0.45	0.36	-	>0.81	-	20.9	0.90	0.61	-	>1.51	-
19.6.80	95.3	0.30	0.27	0.13	0.70	0.67	101.2	0.27	0.36	0.12	0.75	0.76
26.6.80	45.7	0.22	0.11	0.15	0.48	0.22	45.0	0.30	0.13	1.02	1.45	0.65
1.7.80	53.8	0.09	0.11	0.39	0.59	0.32	48.3	0.10	0.10	0.01	0.21	0.10
10.7.80	11.5	0.64	0.23	-	>0.87	-	11.6	-	-	-	-	-
17.7.80	28.5	-	-	-	-	-	23.2	0.10	0.26	-	>0.45	-
23.7.80	51.1	0.17	0.09	0.04	0.30	0.15	53.8	0.20	0.14	0.13	0.47	0.25

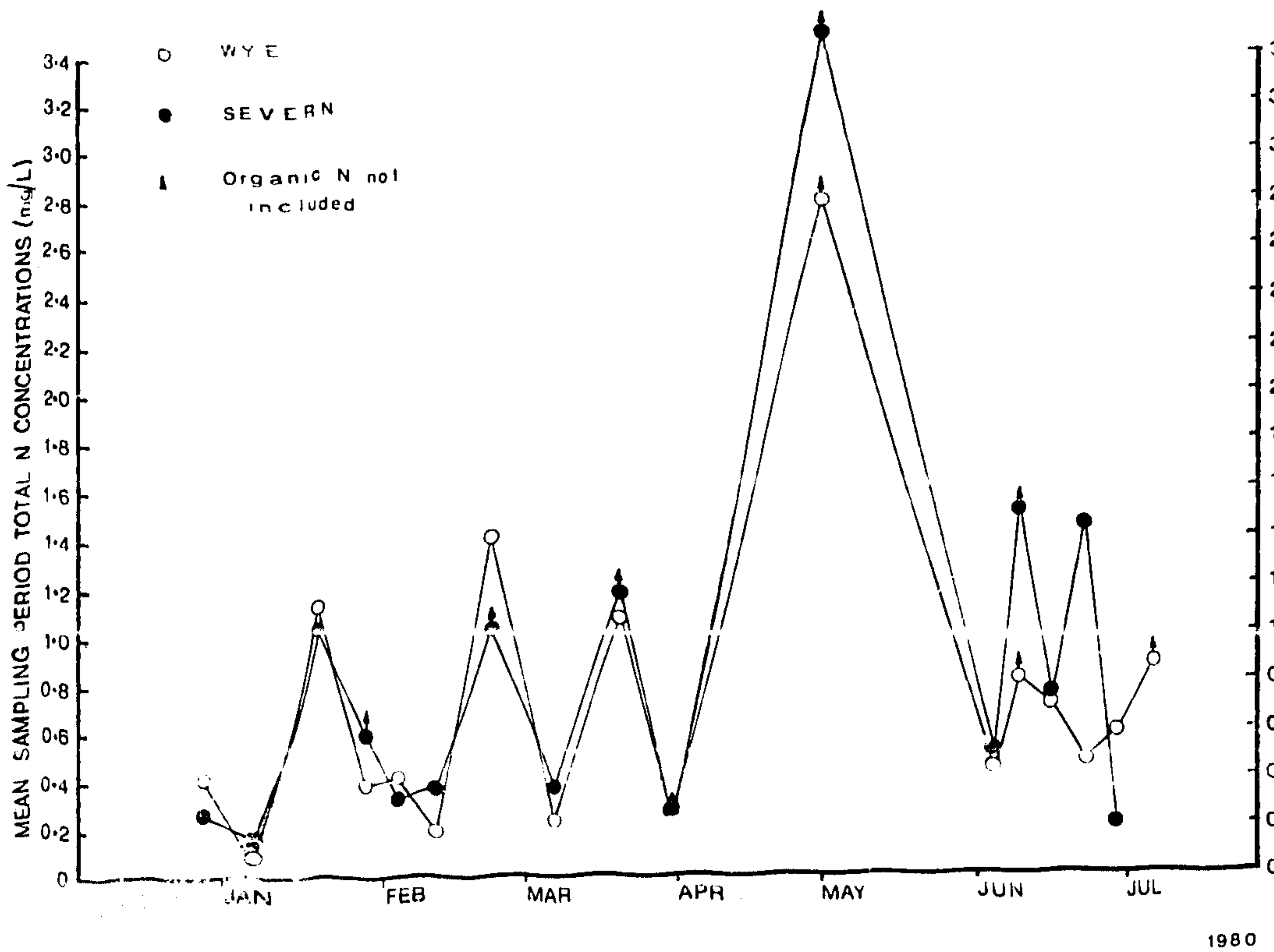


FIGURE 6 Total N concentrations in rainfall samples at Plynlimon

Severn rainfall during 1980 (3.45 mg/l) is matched by a similar high concentration (2.79 mg/l) in the Wye rainfall. This may be typical of inputs during long dry summer periods when ammonia, especially, and oxides of nitrogen accumulate in the atmosphere to be washed out later by small amounts of rain. The occurrence of high nitrate-N concentrations in some samples is probably due to oxidation of ammonium-N during storage; for this reason it is more instructive, when calculating nitrogen balances, to use total nitrogen concentrations rather than the constituent parts. In terms of the nitrogen balance, inputs from samples such as these do not stand out because the high concentrations are balanced by low total rainfall. This gives a reasonably even distribution of input (Fig. 7) over the study period with no obvious seasonal pattern, although including a number of apparently anomalous monthly totals.

It seems therefore that small but significant random errors are introduced into the nutrient balance by a lack of spatial information on nutrient concentrations in rainfall; these errors are impossible to quantify for most of the study period because of a lack of replicate samples. The sampling from two sites in 1980 shows the value of being able to compare the concentrations of individual nitrogen species and isolate the causes of differences between the two samples; contamination usually shows up as a high concentration of soluble organic nitrogen in only one sample.

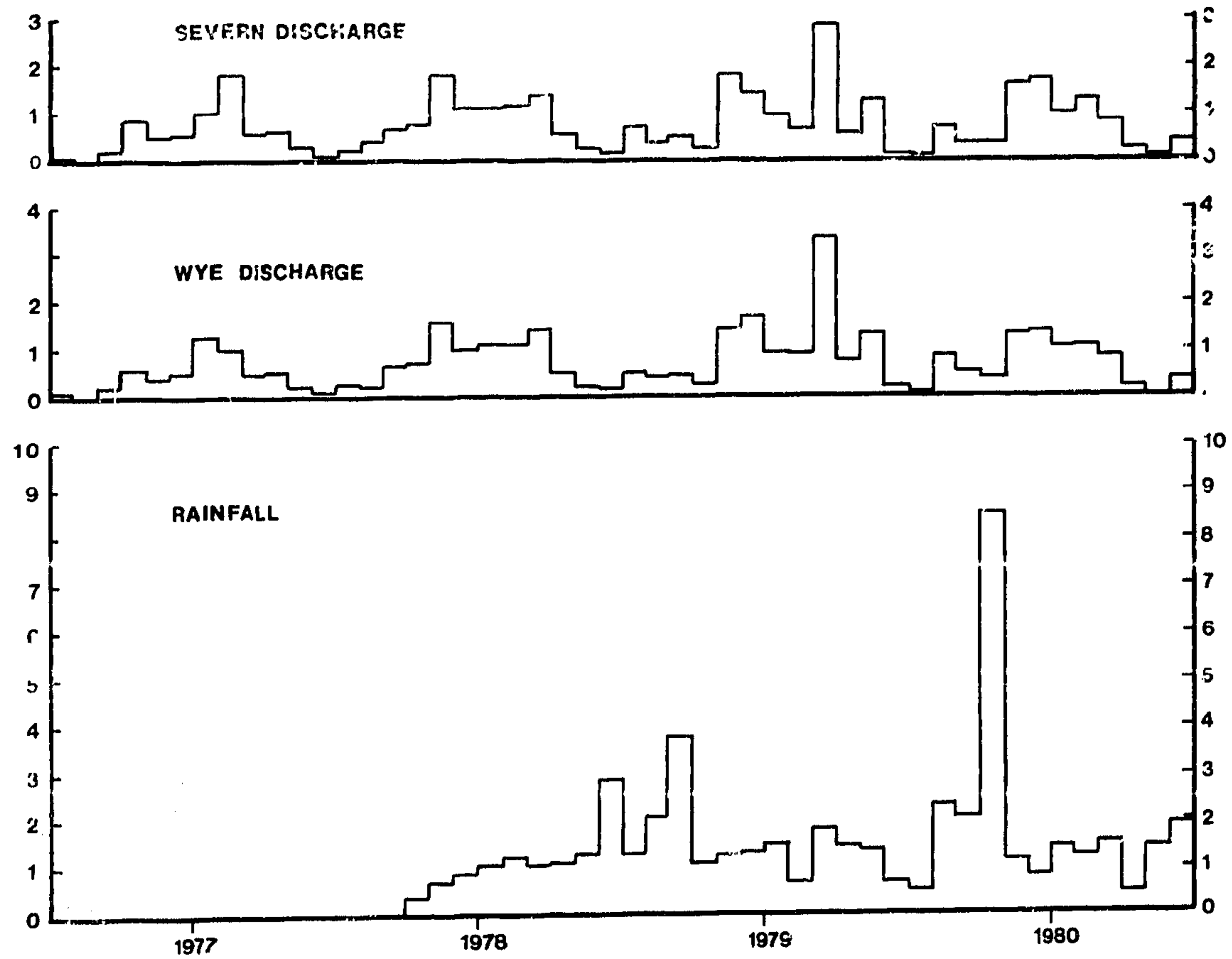


FIGURE 7 Monthly total N inputs and outputs (kg/ha)

3.2 Nutrient loadings in rainfall and runoff

Monthly nutrient loadings in rainfall and runoff are presented in Table 3 and graphically, for total N, in Fig. 7. A graphical display of the differences between monthly nitrogen inputs in rainfall and outputs in streamflow is given in Fig. 8. Annual summaries for all nutrients are shown in Table 1. Discussion of their significance is better accomplished in terms of nutrient balances (section 3.3) but the general pattern for all nutrients can be summarized as being similar to concentration but modified by the inherent seasonality of the rainfall.

3.3 Nutrient balances for the Wye and Severn catchments

Before a nutrient balance is attempted, it may be instructive to briefly review the processes occurring within a nutrient cycle, emphasising those that can be measured or estimated, so as to clarify the concept of a nutrient balance. In terms of the number and complexity of processes occurring, the nitrogen cycle is much more complicated than that of potassium or phosphorus and it is this cycle that has received most attention in the literature. Most of the inputs and outputs are common to all three cycles, however. Fig. 9 shows the various inputs to and outputs from the nitrogen cycle and summarizes the mechanisms by which the

TABLE 3 MONTHLY NUTRIENT LOADINGS (KG/HA) IN THE RAINFALL AND THE DISCHARGES OF THE WYE AND SEVERN AT PLYNLIMON

		RAINFALL			WYE DISCHARGE			SEVERN DISCHARGE		
YEAR/MONTH		N	P	K	N	P	K	N	P	K
1976	JULY	-	-	-	0.07	0.01	0.10	0.07	0.01	0.05
	AUG	-	-	-	0.01	0.00	0.03	0.02	0.00	0.02
	SEPT	-	-	-	0.19	0.01	0.22	0.21	0.01	0.11
	OCT	-	-	-	0.58	0.03	0.48	0.88	0.03	0.34
	NOV	-	-	-	0.42	0.04	0.34	0.51	0.02	0.48
	DEC	-	-	-	0.47	0.03	0.29	0.57	0.02	0.24
1977	JAN	-	-	-	1.31	0.02	0.54	1.03	0.02	0.38
	FEB	-	-	-	1.00	0.05	0.81	1.82	0.03	0.72
	MARCH	-	-	-	0.49	0.02	0.32	0.57	0.01	0.21
	APRIL	-	-	-	0.51	0.03	0.25	0.60	0.03	0.13
	MAY	-	-	-	0.22	0.02	0.15	0.27	0.01	0.12
	JUNE	-	-	-	0.10	0.01	0.06	0.07	0.01	0.03
	JULY	-	-	-	0.26	0.03	0.24	0.21	0.01	0.15
	AUG	-	-	-	0.19	0.01	0.12	0.40	0.01	0.18
	SEPT	-	-	-	0.65	0.02	0.41	0.68	0.02	0.30
	OCT	0.40	0.06	0.33	0.71	0.02	0.49	0.78	0.02	0.38
	NOV	0.72	0.10	0.58	1.62	0.07	0.93	1.82	0.10	0.45
	DEC	0.87	0.02	0.34	0.97	0.05	0.60	1.11	0.03	0.39
1978	JAN	1.06	0.03	0.37	1.11	0.02	0.54	1.09	0.03	0.47
	FEB	1.25	0.02	0.20	1.11	0.03	0.42	1.15	0.05	0.40
	MARCH	1.06	0.03	0.61	1.44	0.04	0.90	1.37	0.04	0.56
	APRIL	1.12	0.02	0.23	0.51	0.01	0.27	0.54	0.02	0.29
	MAY	1.33	0.04	0.21	0.21	0.01	0.13	0.24	0.01	0.13
	JUNE	2.89	0.05	0.67	0.17	0.01	0.09	0.14	0.00	0.07
	JULY	1.31	0.05	1.15	0.50	0.03	0.36	0.71	0.02	0.61
	AUG	2.10	0.01	0.20	0.40	0.03	0.18	0.38	0.02	0.24
	SEPT	3.79	0.03	0.37	0.44	0.03	0.23	0.49	0.03	0.14
	OCT	1.13	0.04	0.26	0.24	0.01	0.14	0.24	0.01	0.10
	NOV	1.25	0.04	0.37	0.37	0.04	0.65	1.79	0.04	0.41
	DEC	1.32	0.03	0.38	1.71	0.06	0.70	1.39	0.04	0.46
1979	JAN	1.53	0.02	0.20	0.92	0.03	0.42	0.95	0.01	0.27
	FEB	0.68	0.01	0.08	0.89	0.02	0.49	0.64	0.01	0.17
	MARCH	1.79	0.04	0.67	3.36	0.04	1.17	2.86	0.10	0.75
	APRIL	1.44	0.01	0.18	0.75	0.01	0.27	0.57	0.01	0.15
	MAY	1.35	0.04	0.41	1.30	0.03	0.36	1.25	0.04	0.26
	JUNE	0.69	0.01	0.18	0.17	0.01	0.09	0.12	0.00	0.05
	JULY	0.48	0.01	0.12	0.05	0.00	0.05	0.04	0.00	0.03
	AUG	2.35	0.07	0.46	0.86	0.03	0.29	0.73	0.02	0.21
	SEPT	2.04	0.05	0.33	0.53	0.02	0.28	0.36	0.02	0.15
	OCT	8.47	0.09	2.51	0.37	0.01	0.39	0.35	0.02	0.12
	NOV	1.17	0.14	0.36	1.29	0.04	0.55	1.59	0.06	0.42
	DEC	0.77	0.11	0.6[illegible]	1.37	0.04	0.68	1.68	0.05	0.54
1980	JAN	1.36	0.02	0.21	1.00	0.02	0.41	0.96	0.02	0.33
	FEB	1.23	0.03	0.33	1.07	0.04	0.79	1.32	0.03	0.57
	MARCH	1.51	0.04	0.20	0.81	0.02	0.43	0.79	0.02	0.22
	APRIL	0.44	0.01	0.28	0.15	0.01	0.09	0.20	0.01	0.08
	MAY	1.41	0.04	0.84	0.03	0.00	0.03	0.03	0.00	0.02
	JUNE	1.89	0.16	0.56	0.32	0.02	0.29	0.41	0.01	0.18

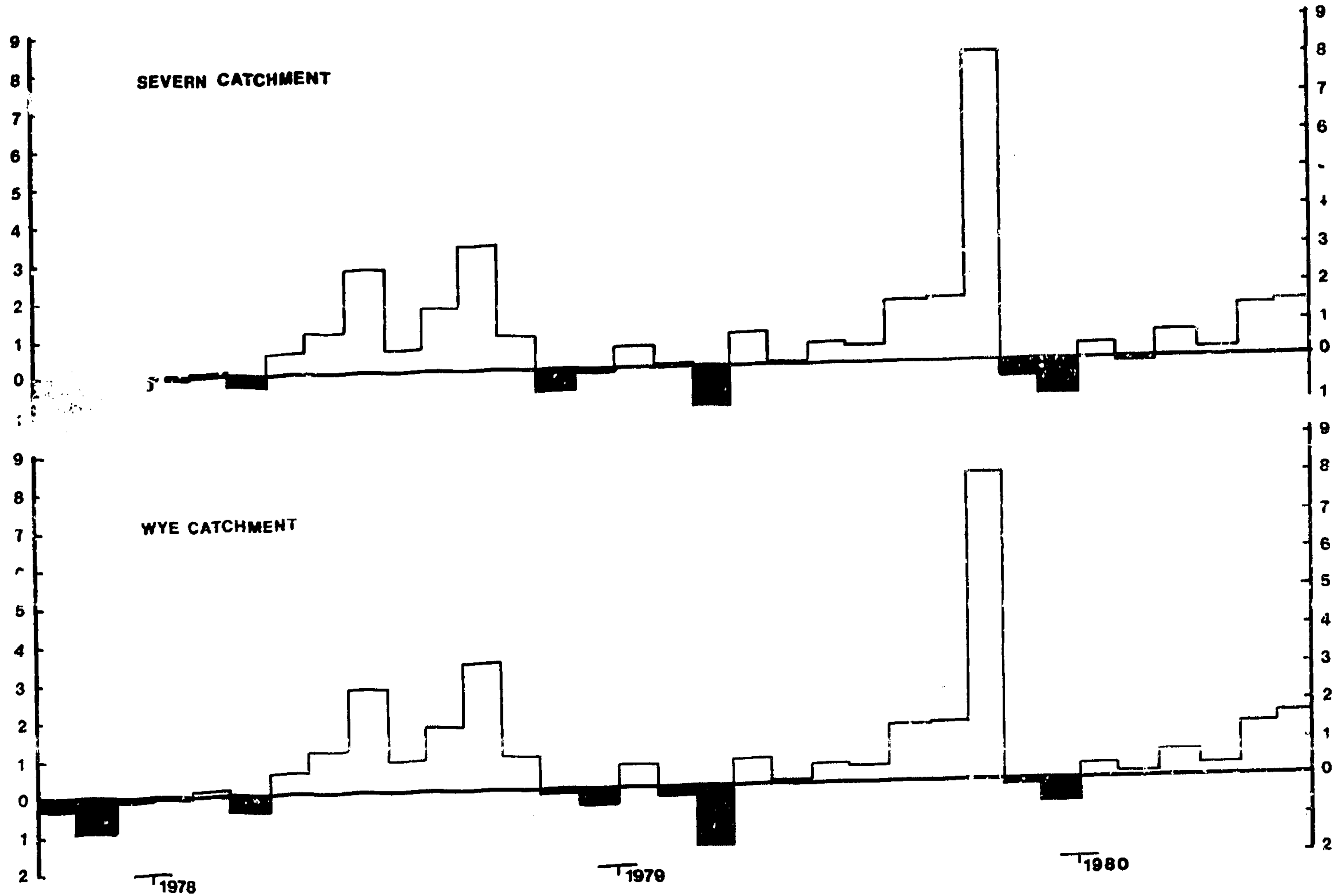


FIGURE 9. Differences in monthly total N loadings (kg/ha) in the rainfall and discharges of the Wye and Severn

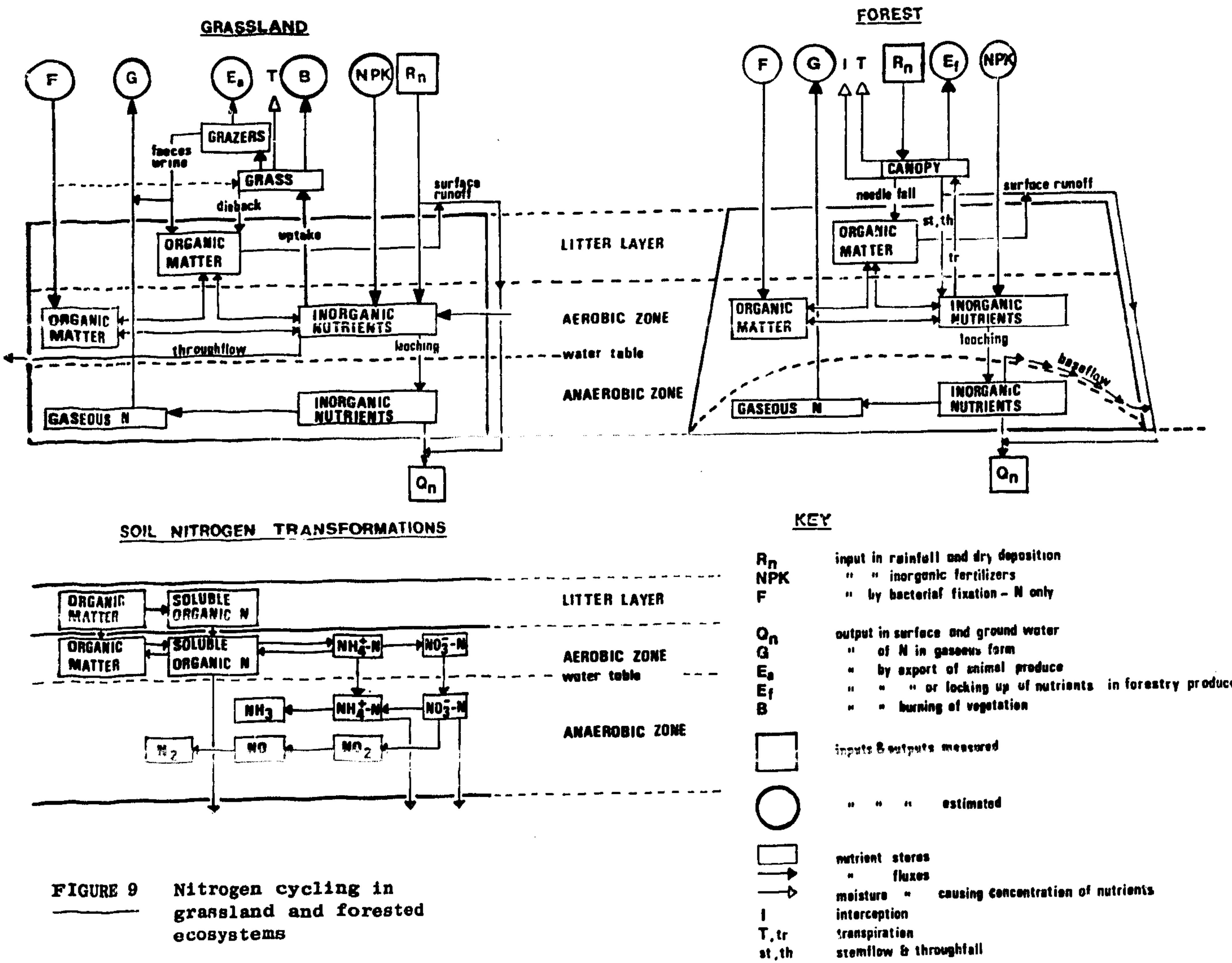


FIGURE 9 Nitrogen cycling in grassland and forested ecosystems

various forms of nitrogen move through the soil/vegetation system. Input to the nitrogen cycle is in rainfall and dry deposition, in inorganic fertilizers, manures and slurries, and as nitrogen fixed by free living and symbiotic organisms. The nitrogen input may be in both the organic and inorganic, ammonium-N and nitrate-N, forms. If in the organic form it must be converted, or mineralized, into the soluble inorganic form before it can take an active part in the soil/vegetation cycle. The fate of the inorganic nitrogen in the soil depends on its concentration and oxidation state, the temperature, pH and water content of the soil solution, the presence or absence of the organisms capable of nitrogen transformations, and the nitrogen demand of growing plants.

During the growing season, most of the available nitrogen will be absorbed, mostly as nitrate-N but also as ammonium-N in acidic soils, by the plants. Some of this nitrogen will leave the cycle in plant and animal agricultural products or, in the case of forests, by being fixed in plant tissues. The rest will be recycled into the soil system as organic matter in plant residues, faeces, urine and leaf fall. In some cases, nitrogen will be lost by the burning of accumulated vegetation and plant stubble.

When the nitrogen demand of plants is low or when availability exceeds demand as in the case of excessive use of inorganic fertilizer, the available nitrogen may be lost to the system by being leached beyond the rooting zone and subsequently into streamflow and groundwater. Alternatively, nitrogen may be lost by being converted to its various gaseous forms and escaping through the soil surface, or by being fixed into the soil organic matter. Nitrogen demand in periods of low availability may be met by the conversion of soil organic nitrogen into inorganic nitrogen. Conversely, nitrogen returned to the soil system by the various processes outlined above may be immobilized within the soil organic matter during periods of low nutrient demand. Thus an internal nutrient cycle exists in the soil system; the nutrient store being depleted during the growing season when demand is high and enhanced during the non-growing season when demand is low. Although the quantity of nutrients involved in this internal cycle is very low compared with the total reserves of nutrients within the soil, nevertheless any imbalance within this cycle will have a profound effect on the overall nutrient balance.

Until more is known of the quantitative biochemistry of the nutrient transformations in the soil/vegetation system, it is possible only to treat the system as a "black box" in which the nutrient inputs to and outputs from the catchments, expressed in units of kg/ha/yr, can be equated thus:

$$\Delta N = R_N - Q_N + NPK + F - G - E - B$$

where ΔN = change in nutrients in total soil component over accounting period;
R_N = input of nutrients in rainfall and dry deposition;
Q_N = loss of nutrients in surface and ground waters;
NPK = input of nutrients in inorganic fertilizers, farmyard manure, slurries and slag;
F = input in nitrogen fixation;
G = gaseous loss of various nitrogen forms;
E = loss of nutrients in net export of agricultural products from the catchment;
B = loss of nutrients due to burning vegetation.

In this particular study, the variables Q_N and R_N have been measured; losses of nutrients to groundwater are negligible in Plynlimon and it is assumed that all the nutrients leached beyond the rooting zone emerge in the streams. The rainfall samples were unfiltered and can be assumed to include any dry deposition as well as the nutrients dissolved in the rainfall. However, this may well lead to an over-estimation of nutrient input by the inclusion of wind-blown dust particles from other parts of the catchment and by contamination, as discussed in section 3.1.

Another possible source of nutrient input to the catchment, denoted by NPK in the balance equation, is in the form of applied fertilizers. Nitrogen is not used on the reseeded areas of the Wye catchment although some basic slag is spread each year and this will affect the phosphorus balance. In this particular study the calculation of the phosphorus balance is not pursued to any degree of accuracy because of the lack of precision inherent in the analysis of phosphorus in solution at low levels. An aerial application of phosphorus and potassium was made to the forested areas of the Severn catchment in 1974. It is assumed, however, that any residual effects of this application on water quality will be insignificant and can be ignored. For these reasons the value of NPK, the input of nutrients in applied fertilizers, has been set to zero in the balance of both catchments. Similarly, the value of B, the loss of nutrients due to the burning of vegetation, has been set to zero for both catchments as this practice is not carried out in the Plynlimon area.

The four other variables in the balance equation have to be estimated and can only, at best, be expressed as a range of values. Probably the easiest term to estimate is E, the net export of agricultural produce. For the Wye catchment this consists of the export of sheep and wool whilst for the Severn catchment some allowance must be made for the nutrients fixed in the tissues of trees on an annual basis. In both cases, these losses are a very small proportion of the annual nutrient uptake; the remainder is returned to the soil as indicated previously (Floate, 1970; Stenlid, 1958).

Crisp (1966) used data on the chemical composition of sheep and their wool from a number of authors and expressed the total export of nutrients as a range of values covering estimates given in the literature. A breakdown of the estimation of the export of nutrients in agricultural produce from the Wye catchment is given below.

Total number of ewes = 2500 in 1055 ha
Number of lambs at approximately 80% lambing rate = 2000

Meat

1750 lambs @ 16 kg live weight sent to market = 28,000 kg
250 ewes @ 30 kg live weight sent to market = 7,500 kg

Total export in live weight 35,500 kg

Export of N @ 0.02 → 0.03 kg N/kg live weight = 0.673 → 1.009 kg N/ha/year
Export of P @ 0.0036 → 0.0090 kg P/kg live weight = 0.121 → 0.303 kg P/ha/year
Export of K @ 0.001 → 0.015 kg K/kg live weight = 0.034 → 0.050 kg K/ha/year

Wool

2250 ewes @ 1.5 kg wool/ewe = 3,375 kg wool
Export of N @ 0.054 → 0.165 kg N/kg wool = 0.173 → 0.525 kg N/ha/year
Export of P @ 0.004 kg P/kg wool = 0.0013 kg P/ha/year
Export of K @ 0.047 → 0.052 kg K/kg wool = 0.150 → 0.166 kg K/ha/year

Totals

Total export of N = 0.85 → 1.54 kg/ha/yr

Total export of P = 0.12 → 0.30 kg/ha/yr
Total export of K = 0.18 → 0.22 kg/ha/yr

The actual values for the Wye catchment will probably be towards the lower ends of the ranges calculated as Welsh hill sheep are generally smaller than the Swaledales studied by Crisp. However, these values are typical of the range of values quoted for the nutrients exported from the upland hill sheep farming areas (Newbould and Float, 1977; Batey, 1982).

Many estimates have been made of the annual rate of accumulation of nutrients in trees, usually during studies on the effect of fertilizers on growth. The rate of accumulation depends on a variety of factors: tree species, soil type and nutrient status, climate and, most importantly, fertilizer rate. Of the estimates quoted in the literature the most appropriate to this study is probably the one by Miller *et al*, 1976, for Corsican pine receiving no fertilizer treatments. They calculated mean annual increases in accumulation over a three year period of 6 kg/ha N, 2.5 kg/ha P, and 8 kg/ha K.

Information on the other three terms in the balance, ie. nitrogen fixation, changes in nutrient content of the soil, and gaseous loss, is very sparse, especially for upland areas. Most of the research has concentrated on lysimeters and soil columns receiving large rates of fertilizers and it is difficult to apply the results obtained from these experiments to field situations particularly in upland areas. The only certain fact is that these gains and losses will be much lower in upland areas than those obtained in the laboratory and in field experiments where high rates of fertilizers are applied. However, compared with the other terms in the balance, these rates may be significant and therefore the most appropriate values quoted in the literature will be used.

A large range of values has been quoted for nitrogen input by biological fixation under different climatic conditions and cropping systems. The highest rates (up to 400 kg/ha N) have been quoted for bacteria living in symbiosis with leguminous plants. In the uplands the low temperatures and acidic conditions inhibit the growth of legumes and any nitrogen fixation occurring will be by free-living bacteria and blue-green algae. Their growth is also restricted by low temperatures, acidic conditions and the supply of suitable energy sources and it is unlikely that the rate of 5-10 kg/ha quoted for upland pastures containing no clover (Newbould and Floate, 1977) will be surpassed in the Wye catchment. The range of values quoted for nitrogen fixation in forested systems is also large. Newbould and Floate (1977) quote a figure of 100 kg/ha for a mixed deciduous woodland derived from laboratory studies, whilst studies in central Europe and the USA quote rates of between 0 and 10 kg/ha (Frizzel, 1977). Bearing in mind the restrictions to bacterial growth imposed by the climatic and soil conditions in the uplands, the same range of values (5-10 kg/ha/yr) has been used for nitrogen fixation for the forested catchment as was used for the grassland catchment.

Most researchers are agreed that the loss of the various gaseous forms of nitrogen from upland areas is negligible. The conversion of nitrate-N to nitrogen gas and the oxides of nitrogen by biological reduction is inhibited by low nitrate-N concentrations, low pH and low temperature, three conditions which are commonplace in upland areas. In some waterlogged areas of the Wye catchment gaseous loss may well occur especially during hot, dry periods and this process has been suggested as one possible reason for the low nitrate-N concentrations in the Wye during the summer and autumn of 1976 (see section 4.1.2). However, these areas are small compared with the total area of the Wye catchment and the amount of time during which the temperatures are sufficiently high so that gaseous loss can occur are short. This means that this process is unlikely to be significant on an annual basis over the whole catchment. It is possible that losses of nitric oxide could occur by the decomposition of nitrite-N but since this species is transient and present in such low concentrations, this process can also be neglected. Appreciable ammonia losses may occur from decomposing faeces and urine especially in the vicinity of sheep pens but since the stocking density is so low, even these losses will be negligible on a catchment basis. Therefore, the gaseous loss of nitrogen has been set to zero for both the grassland and forested catchments.

Perhaps the most difficult variable in the nutrient balance equation to quantify is ΔN, the change in the nutrient content of the soil. Very little data are available in the literature because of the areal variability of soil nutrient content and the difficulty in obtaining consistent results. Under a given soil management system, it is likely that a nutrient equilibrium will be established after several years. However, even a very small percentage change in the nutrient content of the soil will have a profound effect on the nutrient balance, especially of upland areas. For these reasons, no value has been attributed to ΔN. Instead, the values attributed to the other variables of the nutrient balance equation are used to predict ΔN for both the grassland and forested catchments. This is done in Table 4 using average values for 1978/79 and 1979/80. (The values of the nutrients fixed within the trees in the Severn catchment have been modified to account for the fact that the catchment is only 70% afforested, the remaining 30% is assumed to be rough grazed at the same stocking density as the Wye catchment).

Included in Table 4 are nutrient balances cited in Frizzel (1977) from similar agricultural situations to those of the Wye and Severn catchments. As shown, there are large differences in the balances for the various ecosystems, particularly those of nitrogen and potassium. There are several reasons for these differences. In the case of the grassland studies (Wye catchment, Newbould and Floate - 1 and 2), the differences are manifest in the apparent large nitrogen input to the Wye catchment and the apparent large loss of potassium from the Newbould and Floate study areas. The differences are due to the relative values of nitrogen and potassium inputs in rainfall and dry deposition and the outputs by runoff. In the Wye catchment nitrogen input in rainfall and dry deposition was found to be much greater than the output in the streamflow, whereas Newbould and Floate suggested the opposite in their study. It may well be the case that the amount of nitrogen input in rainfall to the Wye catchment may be overestimated as has been suggested earlier. On the other hand, the nitrogen input and output data used by Newbould and Floate have been obtained using reports from other upland areas in Britain and may not be totally applicable to the area under consideration. A similar reason is found for the discrepancies in the potassium balance; for the Wye catchment the inputs and outputs are balanced while for the studies of Newbould and Floate the output in leaching and runoff greatly exceeds the input in rainfall and dry deposition.

Similar differences are seen when comparing the Severn catchment and the forested ecosystems in central Europe and the USA (Ulrich - 2, Thomas and Gilliam - 7 and 8). In these cases the differences are caused by bigger values for the immobilization of nutrients in the trees (output of primary products) for both the American and central European studies and the neglect of nitrogen fixation for the European and one of the American studies.

The comparisons shown in Table 4 and a review of the various quoted rates of nutrient inputs to and outputs from upland ecosystems demonstrates the paucity of good quality data available to solve the balances of the relatively simple upland nutrient cycles. Obviously much research still remains to be done in the uplands before a full understanding of the various nutrient inputs, outputs and transformations can be achieved.

TABLE 4 NUTRIENT BALANCES FOR THE WYE AND SEVERN CATCHMENTS AT PLYNLIMON USING AVERAGE VALUES (kg/ha/annum) FOR 1978/79 AND 1979/80

	WYE CATCHMENT			SEVERN CATCHMENT		
	N	P	K	N	P	K
R_N	+20.8	+0.6	+5.6	+20.8	+0.6	+5.6
Q_N	-10.0	-0.3	-7.2	-10.0	-0.3	-3.2
NPK	-	-	-	-	-	-
F	+ 7.5	-	-	+ 7.5	-	-
G	-	-	-	-	-	-
E	- 1.2	-0.2	-0.2	- 4.6	-1.8	-5.7
B	-	-	-	-	-	-
ΔN	+17.1	+0.1	-1.8	+13.7	-1.5	-3.3
Newbould & Floate (1) **High elevation moorland, sheep, UK**	+ 2.0	-0.7	-9.0			
Newbould & Floate (2) **Traditional hill sheep farming, UK**	+ 2.0	-0.3	- 6.0			
Ulrich (2) **Coniferous forest on grey-brown podzolic soil, Central Europe**				0	-0.6	+1.0
Thomas & Gilliam (7) **Loblolly Pine, 40 years, Mississippi, USA**				+ 2.4	-0.5	-8.3
Thomas & Gilliam (8) **Douglas Fir, 37 years, Washington, USA**				- 4.3	-1.4	-8.5

3.4 Upland stream concentrations in the wider, drainage basin context

For the results of this monitoring exercise to have any practical benefit, it is important to understand the contribution in terms of quantity and quality, of upland runoff to the resources of the downstream user. Most of the water available in these basins is abstracted from the lower reaches; however, the great contributions in quality and quantity of the upper reaches to this resource belie their small catchment areas.

The differences in source area type are manifest in the reported levels of nutrients at abstraction points nationwide. Walling and Webb (1981) present a map of the most polluted rivers in Britain. Most of the pollutant load stems from industrial waste, though sewage and agricultural runoff has turned relatively pristine upland streams such as the Tyne into heavily polluted rivers even before industrial influences are added. The Severn and the Wye for most of their length are classed as unpolluted though the Avon tributary of the Severn has doubtful to grossly polluted stretches, whilst the Wye below Hereford is termed poor before its confluence with the River Lugg results in a return to its unpolluted state. Clearly, in terms of nitrate concentration, neither catchment can compare with the heavily polluted rivers in eastern England such as the Trent and Yoxall with 9.3 mg/l average and the Bedford Ouse with 11.33 mg/l, the latter exceeding the World Health Organisation limit of 11.3 mg/l for nitrate-N in drinking water. Fig. 10 and Table 5 indicate the mean annual concentrations of nitrate-N,

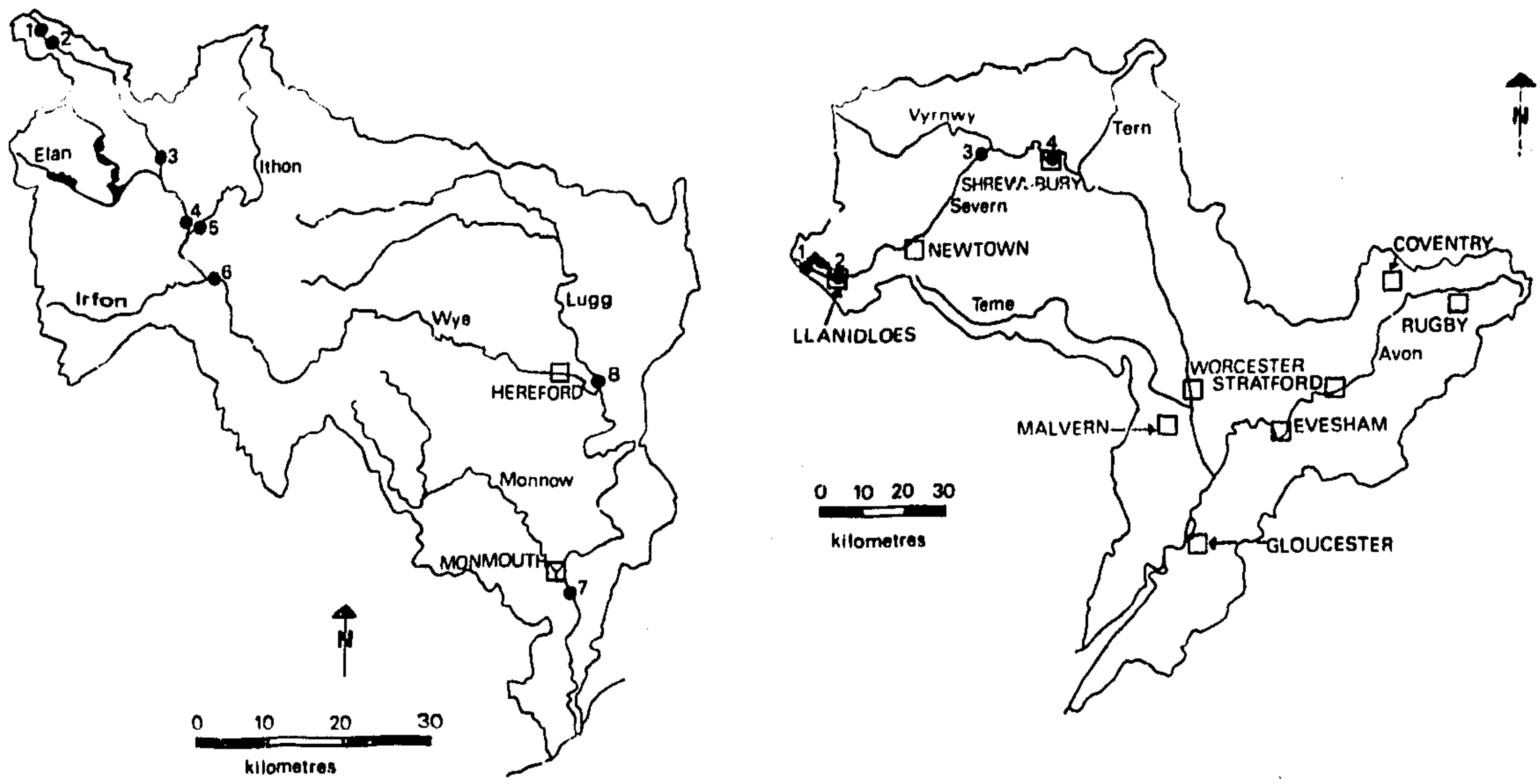


FIGURE 10 Sampling points in the Wye and Severn basins

TABLE 5 Nutrient concentrations at selected points along the Wye and Severn (see Figure 10 for sampling sites)

SEVERN

No.	Site Name		TOTAL N (mg/L) MAX	MEAN	MIN	TOTAL P (mg/L) MAX	MEAN	MIN	TOTAL K (mg/L) MAX	MEAN	MIN	pH MAX	MEAN	MIN
1	SEVERN TRAPEZOIDAL FLUME	*	1.64	0.40	0.11	0.12	<0.01	<0.01	1.00	0.18	0.06			
2	LLANDLOES	†	1.80	0.80	0.05	0.1	<0.01	<0.01				9.25	6.7	4.80
3	LLANDRINIO	†	6.00	2.20	0.35	2.9	0.1	<0.01				8.3	7.3	4.95
4	[illegible]TON (SHREWSBURY)	†	15.00	2.40	<0.1	0.98	0.1	<0.01	13.0	2.2	1.0	9.5	7.5	6.15

WYE

No.	Site Name		NO_3^--N(mg/L) MAX	MEAN	MIN	PO_4 - P(mg/L) MAX	MEAN	MIN	TOTAL K (mg/L) MAX	MEAN	MIN
1	CEFN BRWYN WEIR	*	0.75	0.18	0.01	0.06•	0.015•	<0.01•	0.84	0.21	0.02
2	PANT MAWR	Δ	0.70	0.11	0.01	0.10	0.006	<0.005		0.37	
3	ABOVE ELAN CONFLUENCE	Δ	1.30	0.59	0.01	0.12	0.010	<0.005		0.69	
4	ABOVE ITHON CONFLUENCE	Δ	1.50	0.49	0.01	0.10	0.008	<0.005		0.55	
5	RIVER ITHON	Δ	3.00	1.10	0.02	0.50	0.092	0.01		2.11	
6	BELOW IRFON CONFLUENCE	Δ	2.50	0.72	0.01	0.12	0.018	<0.005		0.92	
7	BELOW MONNOW CONFLUENCE	Δ	5.00	3.23	0.01	0.36	0.122	0.05		2.34	
8	RIVER LUGG	Δ	7.00	3.76	0.02	0.48	0.152	0.02		3.08	

* All samples taken on an 8-hourly basis compared to a weekly basis at other sites. Maximum and minimum values more likely therefore to be extreme values. Period July 1976 - June 1980.

† Period for nitrogen 1976-1980 and for other species 1975-1980; data taken from Severn-Trent Water Authority monitoring scheme.

Δ All values the mean of two annual means from September 1975 - August 1976 and September 1976 - August 1977 but not flow weighted; data taken from Oborne et al (1980).

• Refers to Total P not PO_4^+ - P.

phosphorus and potassium as [illegible] the statutory Harmonized Monitoring Scheme with the levels at Plynlimon for comparison. It seems that the Severn and Wye, though both heavily used in their lower reaches, particularly the Severn, have managed to keep nitrate-N, phosphate and potassium concentrations to reasonable levels. This difference is mainly due to the amount of fertilizers used in eastern England where large amounts of NPK are needed for cereal growth compared to that applied to grassland in the livestock-orientated farming of the Wye and Severn valleys, the Avon tributary being the exception. The contribution of relatively clean runoff from the upland source areas of Wales must also give an advantage to the Severn and Wye over their eastern, lowland source area counterparts.

Although yields of grass and arable crops can be enhanced dramatically by the increased use of fertilizer, high energy costs have rendered it impractical to apply extra if the return does not match the investment. It is mainly in the upland areas of Britain that increased production, of both timber and agricultural produce, can be obtained by land-use change, improvement and judicial use of fertilizer. If this happens, water quality will almost certainly deteriorate. Although concentrations are unlikely to even approach levels already commonplace downstream, because of the lower fertilizer application rates and higher rainfall, the role of large volume upland runoff as a dilution agency could be curtailed. Any such curtailment may have substantial financial implications for water supply.

4 FURTHER ANALYTICAL OBJECTIVES

Because of the seasonal variation and differences in nitrate-N concentrations in the streamflows of the Wye and Severn, most of the following discussion is concerned with nitrogen. However, some aspects also apply to potassium and phosphorus though, in the case of the latter, the concentrations were so often below the limit of detection that meaningful analysis was rendered impossible.

4.1 Suggested explanations of the general patterns in stream nutrient concentrations

4.1.1 General trends in nutrient losses from upland catchments

In the absence of long term data on nutrient concentrations in rainfall and streamflow emanating from upland catchments, we can only assume that because the agricultural framework of areas such as the Wye catchment has remained relatively unchanged for several hundred years (with the exception of small scale grassland improvement in the 1930s) such catchments are in a state of long term equilibrium with respect to inputs and outputs of nutrients. Clearly stream nutrient levels do oscillate within this long-term stability, as a result of a combination of short term (annual) fluctuations in input concentrations and the complex interaction of stores and fluxes within the system.

Over any annual period there is an order of magnitude parity between inputs in rainfall and outputs in streamflow. Rainfall samples collected in the summer months April — October exhibit higher concentrations than in the winter months, a phenomenon also reported by other workers (Ångström and Högberg, 1952, and Eriksson, 1952). The relatively high pH values in the rainfall samples (range 5.5–6.5) precludes industrial pollution as the source of variation of nitrogen in

precipitation; indeed most of the nutrients in rainfall over the mid-Wales uplands have a maritime source (Cryer, 1976). It is also unlikely to be caused by the washout of ammonia released from the breakdown of animal urine in the soil as stocking densities remain fairly constant over the year in such areas. It is possible, therefore, that the accumulation, breakdown and leaching of plant and, especially, animal debris in the collecting funnel causes some, if not all, of the high concentrations. It can be argued that such debris is a real input to the catchments (Whitehead and Feth, 1964) but the propensity of insects for committing suicide in raingauge funnels does not allow realistic areal extrapolation of the results. Filtered rainfall samples collected by other workers at Plynlimon (M. Hornung, ITE, personal communication) show little of the seasonal variation.

Whichever estimate of summer rainfall is taken, two distinct phases emerge - the period between April and October when rainfall concentrations are greater than stream concentrations, and the period between November and March when the reverse is true. There is a good physiological reason for the former state of affairs in that it is during this summer period when evaporation is at its highest. Transpiration is of similar magnitude in both the forested and grassland catchments and is the mechanism by which nutrient rich interstitial water is taken up by plants and stored as biomass. In addition, as the temperature rises, other forms of micro-organismic life begin the task of completing the growth cycle of plants by breaking down plant debris to its constituent parts. In this initial phase all living matter requires a net input of nutrients and in consequence the relatively nutrient rich rain water is depleted before contributing to summer baseflow. Therefore, an upper limit of nutrient concentration in streams in set during the summer months by the concentration in rainfall. Stream water occasionally approaches this value during wet summer periods when nutrient input in rainwater is far in excess of deficit requirements or when rainfall intensity is so great that direct runoff to the stream occurs.

A contributing factor to the very low summer nitrogen concentrations in the discharge of the Wye catchment lies in the biochemical characteristics of waterlogged soils. Even in 1976, a considerable drought by any standards, the mesotrophic mires (valley bottom bogs) of the Wye catchment (Fig. 2) did not dry out appreciably. Anaerobic conditions prevailed in the mires and this, coupled with the high temperatures needed for high rates of micro-organismic conversion of nitrate-N to ammonia and nitrogen gas, depleted much of the available soluble nitrogen causing extremely low values of nitrate-N in the Wye.

In addition, the higher than average ammonium-N concentrations in the runoff during 1976/77 suggested that, as argued in section 3.1, more of the nitrogen in rainfall falls as ammonium-N during dry periods. The direct loss of ammonia from the soil surface before conversion of ammonium-N to nitrate-N may deplete the reserves of soluble nitrate-N available for subsequent leaching and hence the concentrations of nitrate-N in the summer and autumn flow of 1976; unfortunately no rainfall concentration data was available for this period to confirm this speculation.

There are two possible reasons why the very low nitrate-N concentrations in the Wye during the summer and autumn of 1976 were not mirrored in the nitrate-N concentrations of the Severn.

Firstly, the ability of the mesotrophic mires in the Severn, not as extensive as those in the Wye in any case, to lose nitrate-N by denitrification has been destroyed by artificial drainage of those areas to aid sapling establishment. Therefore, the direct runoff of nutrient rich waters from the acidic grassland/podzol soil covered slopes enables the relatively high nitrate-N concentrations in the discharge of the Severn to be maintained.

Perhaps more important, however, is a hydrogeological characteristic of the Severn catchment; the more extensive shallow aquifers and drift deposits hold up the water yield of the Severn catchment more effectively than the Wye catchment. This gave baseflow yields in the Severn which were ten times those in the Wye during the height of the drought. The provision of these extra stores helps to damp year to year variations in the pattern of both water and nitrogen runoff and results in the Severn catchment being less susceptible, in quantity and quality terms, to the deprivations of drought.

In terms of total N loss, the picture is less clear since organic N losses, being higher in the Wye than the Severn in 1976, balances to a certain extent the reduction in nitrate-N. Organic N concentrations are also noticeably more responsive to changes in discharge during 1976 and 1977 than in the later years of the study. Both these phenomena could be manifestations of the desiccation of grassland soils in 1976 encouraging soil erosion by heavy rainfall for a limited period after 1976. Desiccation did not occur in the Severn catchment to the same extent because of the supression of temperatures and shading from direct sunlight afforded by the forest canopy.

The study by Crisp (1966) of the nutrient balance of a small Pennine catchment, Rough Sike, on the Moor House field station, Cumberland, pioneered work in this field of peat erosion. Of the 17.6 kg/ha of nitrogen lost each year in the catchment streamflow, 83% came in the form of eroded peat particles. Clearly, eroding blanket peat constitutes a higher proportion of the Rough Sike catchment than either the Wye or the Severn, nevertheless a certain amount of both catchments is covered by peat and erosion must contribute to the stream nitrogen load. Further evidence is provided by the tendencies of the streams, particularly the Severn which has a higher proportion of blanket peat than the Wye, to turn brown during high flows, and this may help to explain differences in nitrogen loss between the two catchments.

A phenomenon much reported and speculated upon is the increase in nitrogen (and other) concentrations with discharge (Walling and Foster, 1975). To relate this phenomenon wholly to increases in discharge however is misleading, even though correlations of concentration against discharge generally show high positive agreement. Nitrogen concentrations in streams will always show high correlation with those hydrological variables which also vary seasonally in the same way - soil moisture, soil temperature and baseflow, though the relationships may not be causal (Figs 11 and 12). However, any increase in discharge from whatever is the normal baseflow characteristic at the time will cause the flushing out of nitrogen made available in the period since the last time productive horizons were leached. This is particularly so during the warm and relatively dry summer months when substantial quantities of the reduced forms of nitrogen (ammonium-N, nitrite-N and soluble organic N) will be converted into nitrate-N by micro-organisms in the aerobic soil horizons. This view is confirmed by the data (Fig. 4) which show a much larger increase in nitrogen concentrations with increasing discharge when the baseflow is low (summer months) than a corresponding increase in discharge when baseflow is high because, obviously, in the summer months a larger volume of soil remains drier for longer than during the winter months. The culmination of this phenomenon occurs in the autumn of most years when rains following a dry summer period flush out the nitrogen that has been made available.

Taking this argument further, it seems unlikely that sufficient nitrogen is made available during the latter parts of the summer to sustain the high nitrogen concentrations prevalent in winter (Fig. 3). The decrease in use of water and nitrogen by plants in the autumn and winter and the re-allocation of this water to leachate is obviously a contributory factor but cannot alone explain the high

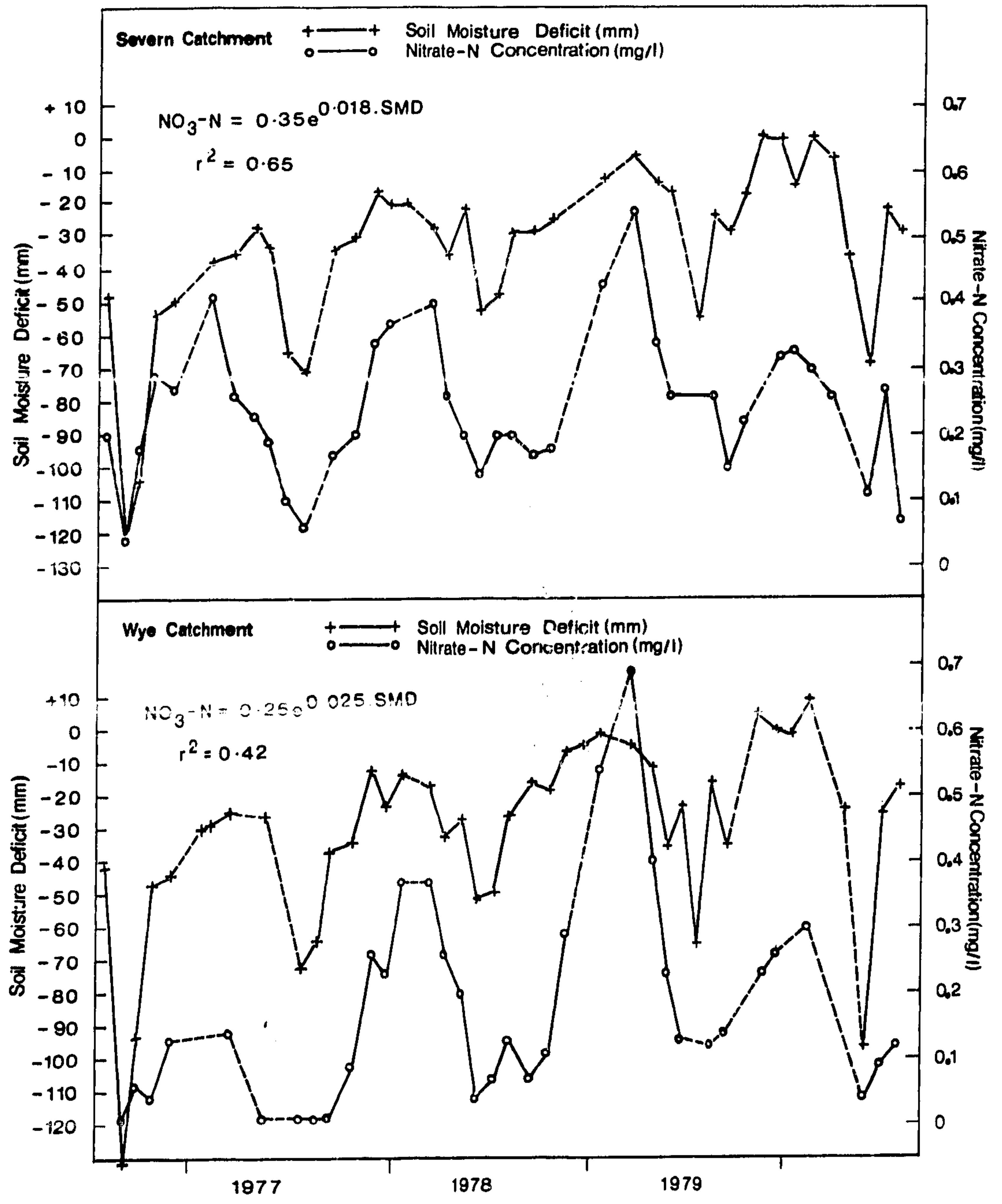


FIGURE 11 Time series graphs of nitrate-N concentrations and soil moisture deficits

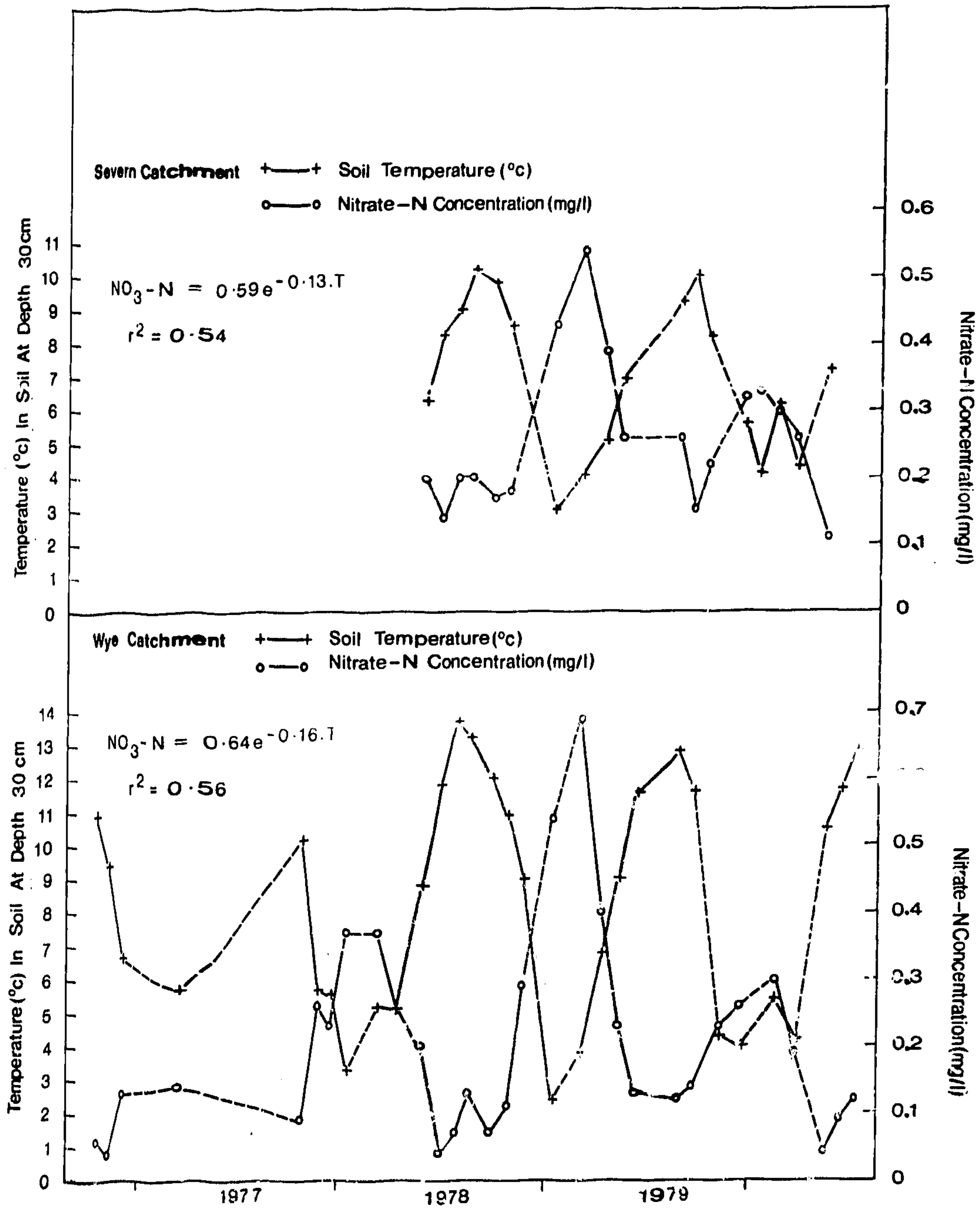


FIGURE 12 **Time series graphs of nitrate-N concentrations and soil temperatures**

nitrogen concentrations in the streamflow as these frequently exceed the concentrations in rainfall.

To fully explain this phenomenon, we must return to the initial argument, that storage and release within the catchment system is the mechanism producing the variation in stream nitrogen concentrations. The process that reduces nitrogen concentrations in summer - transpiration-controlled plant growth - declines during the autumn and is accompanied by dieback which boosts the reserves of soil organic matter. Mineralization is the main biochemical control on mineral nitrogen production and proceeds at a rate determined by a combination of soil temperature, soil moisture, pH and available organic nitrogen (Cassman and Munns, 1980; Stanford and Epstein, 1974). Of these, the latter appears to be the most important factor. The rate of mineral nitrogen production is directly proportional to the amount of available organic nitrogen and can be expressed as:

$$\frac{dN}{dt} = k.S_N \quad \text{where} \quad \frac{dN}{dt} = \text{rate of mineral nitrogen production}$$

S_N = amount of available organic nitrogen

k = exponential constant (t^{-1})

Assuming that stream nitrogen concentrations in winter are directly related to the rate of mineral nitrogen production, the observed peak concentrations in January and February imply that dN/dt also reaches a peak in this period. This in turn implies that S_N is at a maximum not in the autumn but in late winter.

Dieback, therefore, must be a gradual process but occurring at a faster rate than the incubation process can convert organic nitrogen to leachable mineral nitrogen.

This supposition is supported by Job and Taylor (1978) whose studies of grassland production in the Wye catchment indicated that litter fall experiences slow and only partial breakdown. Consequently the percentage of green material in the plant, at a maximum in June or July of each year, senesces rapidly in August and September and declines to a minimum in March the following year. This matches almost identically, but inversely, nitrate-N concentrations in runoff. Unfortunately no production data are available for the study period to test the statistical significance of this.

4.1.2 Within-catchment variation in nutrient losses

Two further studies, conducted for a twelve month period, were initiated at the end of 1979 to try to explain the differences in nutrient, particularly nitrate-N, losses from the two catchments.

(a) Subcatchment nutrient survey

To unravel some of the complexities hidden by the black box approach to comparative nutrient levels in the Wye and Severn catchments, streamflow samples were collected on an irregular time basis at the outlets of discrete subcatchments within the two main catchments and supplemented by nested catchment samples to detect changes in concentrations downstream. The network (Fig. 1) consisted of 11 sites in the Wye and 12 in the Severn, visited monthly. All samples collected during any one visit were taken within 30 minutes of each other to ensure comparability and, with the exception of those on 6.8.80, were taken on the recession limb of the hydrograph so that large changes in discharge did not occur during the sampling period. This practice meant that studies of changes in nutrient concentration with flow rate could not be done; provision for this approach would have entailed a far more frequent and larger sampling programme than was possible within the overall framework of the experiment.

The limitations of the sampling programme when compared to the more detailed main catchment monitoring exercise do not negate comparisons between sub-catchments under the same hydrological and meteorological conditions, restricted as the range of those conditions sampled were over the study period. Too much significance should not be attached to the wider application of the results, though the indications are invaluable for suggesting future research. The results for N, K and pH are shown in tabular form in Tables 6a and 6b and as means and standard errors on a network map in Fig. 13.

TABLE 6A RESULTS OF THE AREAL SAMPLING

DATE	SEVERN ST	LOWER HAFREN TRIBUTARY H1	UPPER HAFREN H2	TANLLWYTH H3	HAFREN H4	UPPER TANLLWYTH H5	UPPER HORE H6	HORE H7	UPPER HAFREN TRIBUTARY H8	HAFREN SOURCE H9	ARWYSTLI H10	HAFREN PEAT HAG PIPE H11	WYE CB	CYFF G1	WYE-CYFF G2	GWRDY G3	GWY G4	IAGO G5	UPPER CYFF G6	COLWYN G7	CYFF SOURCE G8	GERIG G9	UPPER GWY G10
29.11.79	.34	.29	.26	.54	.32	.37	.26	.32	.23	.26	.26	.23	.26	.17	.37	.34	.29	.32	.17	.18	.34	.26	.37
9. 1.80	.34	.23	.30	.37	.29	.29	.29	.33	.26	.29	.27	.23	.29	.20	.37	.32	.34	.29	.23	.19	.40	.34	.45
30. 1.80	.46	.29	.54	.37	.46	.32	.45	.45	.43	.47	.47	.41	.57	.34	.68	.32	.81	.40	.47	.23	.86	.67	.89
5. 3.80	.39	.25	.34	.44	.27	.30	.29	.27	.25	.29	.25	.18	.22	.15	.25	.25	.25	.19	.18	.19	.36	.33	.39
2. 4.80	.30	.23	.27	.32	.27	.25	.22	.25	.25	.27	.25	.25	.25	.16	.27	.19	.30	.19	.15	.11	.25	.27	.45
2. 5.80	.15	.13	.18	.17	.18	.15	.19	.16	.15	.22	.19	.27	.05	.01	.11	.15	.08	.09	.01	.08	.06	.01	.12
4. 6.80	.18	.16	.20	.19	.19	.25	.18	.18	.19	.19	.20	.13	.12	.06	.18	.16	.15	.18	.01	.06	.05	.12	.08
15. 7.80	.13	.12	.18	.11	.15	.11	.15	.13	.10	.15	.16	.06	.04	.01	.09	.13	.06	.08	.01	.06	.01	.01	.09
6. 8.80	.17	.27	.18	.17	.16	.15	.15	.14	.08	.11	.08	.13	.02	.02	.06	.13	.04	.08	.03	.08	.03	.03	.06
30.10.80	.37	.32	.23	.56	.26	.34	.23	.29	.14	.16	.17	.17	.17	.17	.06	.23	.15	.17	.01	.08	.10	.06	.17
9.12.80	.34	.27	.30	.43	.33	.32	.27	.30	.19	.27	.25	.18	.23	.16	.26	.26	.23	.22	.11	.15	.26	.18	.29
MEAN	.29	.23	.27	.33	.26	.26	.24	.26	.21	.24	.23	.20	.20	.13	.25	.23	.25	.20	.13	.13	.25	.21	.30
STD DEV	.11	.08	.11	.16	.10	.08	.10	.09	.09	.11	.10	.10	.16	.10	.18	.06	.20	.10	.14	.06	.25	.20	.25
STANDARD ERROR	.03	.02	.03	.05	.03	.02	.03	.03	.03	.03	.03	.03	.05	.03	.05	.02	.06	.03	.04	.02	.08	.06	.08

NO_3-N (mg/l)

DATE	ST	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	CB	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10
29.11.79	.42	.36	.32	.65	.38	.48	.36	.38	.34	.31	.31	.28	.39	.25	.51	.46	.38	.43	.28	.26	.45	.38	.46
9. 1.80	.43	.29	.41	.54	.42	.40	.35	.42	.39	.38	.33	.28	.40	.28	.48	.43	.43	.37	.34	.28	.48	.42	.54
30. 1.80	.60	.37	.69	.55	.66	.51	.63	.56	.56	.59	.56	.53	.68	.44	.78	.40	1.04	.48	.55	.29	1.03	.79	1.10
5. 3.80	.47	.29	.43	.53	.38	.37	.34	.34	.33	.36	.29	.24	.27	.18	.31	.31	.31	.25	.25	.26	.44	.39	.47
2. 4.80	.34	.27	.34	.39	.33	.34	.28	.29	.36	.35	.31	.28	.34	.24	.36	.26	.36	.26	.22	.17	.34	.34	.53
2. 5.80	.26	.19	.27	.26	.26	.28	.27	.24	.38	.34	.34	.50	.17	.13	-	.30	.12	.17	.11	.14	.13	.10	.21
4. 6.80	.31	-	.30	.29	.25	.32	.24	.25	.30	.27	.26	.21	.36	.22	.21	.32	.22	.26	.09	.12	.11	.19	.15
15. 7.80	.20	.15	.26	.17	.19	.17	.25	.21	.23	.19	.22	.1?	.22	.20	.17	.24	.26	.19	.16	.12	.07	.07	.15
6. 8.80	.31	.48	.37	.52	.33	.55	.33	.31	.56	.29	.30	.30	.16	.22	.28	.35	.22	.28	.23	.28	.14	.14	.17
30.10.80	.54	.43	.31	.74	.40	.45	.32	.37	.28	.24	.21	.21	.26	.33	.25	.29	.25	.31	.11	.18	.15	.16	.26
9.12.80	.49	.40	.46	.68	.58	.48	.40	.45	.39	.43	.39	.31	.36	.27	.43	.43	.39	.36	.22	.26	.41	.29	.43
MEAN	.40	.32	.38	.48	.38	.40	.34	.35	.38	.34	.32	.30	.33	.25	.38	.35	.36	.31	.23	.21	.34	.30	.41
STD DEV	.12	.10	.12	.18	.14	.11	.11	.10	.10	.11	.09	.11	.14	.08	.18	.07	.24	.10	.13	.07	.28	.21	.28
STANDARD ERROR	.04	.03	.04	.06	.04	.03	.03	.03	.03	.03	.03	.03	.04	.02	.06	02	.07	.03	.04	.02	.08	.06	.08

Total N (mg/l)

TABLE 6B RESULTS OF THE AREAL SAMPLING

DATE	SEVERN ST	LOWER HAFREN TRIBUTARY H1	UPPER HAFREN H2	TANLLWYTH H3	HAFREN H4	UPPER TANLLWYTH H5	UPPER HORE H6	HORE H7	UPPER HAFREN TRIBUTARY H8	HAFREN SOURCE H9	ARWYSTLI H10	HAFREN PEAT HAG PIPE H11	WYE CB	CYFF G1	WYE-CYFF G2	GWRDY G3	GWY G4	IAGO G5	UPPER CYFF G6	COLWYN G7	CYFF SOURCE G8	GERIG G9	UPPER GWY G10
29.11.79	.14	.13	.12	.08	.12	.08	.10	.09	.10	.13	.11	.13	.19	.12	.19	.18	.13	.20	.12	.12	.10	.11	.10
9. 1.80	.14	.06	.13	.07	.24	.15	.09	.09	.13	.14	.12	.13	.18	.16	.15	.16	.12	.19	.17	.13	.13	.14	.11
30. 1.80	.18	.09	.22	.10	.20	.12	.15	.15	.16	.21	.24	.21	.21	.18	.22	.20	.22	.21	.21	.14	.16	.21	.22
5. 3.80	.11	.08	.11	.09	.10	.10	.08	.10	.09	.10	.10	.14	.11	.09	.12	.17	.09	.17	.11	.08	.08	.10	.10
2. 4.80	.08	.10	.10	.10	.08	.08	.10	.10	.11	.10	.14	.11	.14	.12	.17	.17	.12	.13	.13	.08	.11	.10	.10
2. 5.80	.14	-	.09	.16	.11	.13	.14	.12	.13	.09	.11	.20	.13	.10	.14	.28	.08	.24	.09	.09	.08	.10	.06
4. 6.80	.17	.07	.16	.19	.15	.17	.10	.13	.16	.11	.11	.10	.44	.67	.41	.26	.16	.30	.50	.12	.05	.11	.10
15. 7.80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
6. 8.80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
30.10.80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
9.12.80	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
MEAN	.14	.09	.13	.11	.14	.12	.11	.11	.13	.13	.13	.15	.20	.21	.20	.20	.13	.21	.19	.11	.10	.12	.11
STD DEV	.03	.03	.05	.05	.06	.03	.03	.02	.03	.04	.05	.04	.11	.21	.10	.05	.05	.05	.14	.03	.04	.04	.05
STANDARD ERROR	.01	.01	.02	.02	.02	.01	.01	.01	.01	.02	.02	.02	.04	.08	.04	.02	.02	.02	.05	.01	.01	.02	.02

K (mg/l)

DATE	ST	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11	CB	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10
29.11.79	5.8	5.0	6.1	5.4	6.1	5.0	6.3	5.8	4.9	5.9	6.1	6.0	6.4	6.5	6.2	6.3	6.0	6.4	6.2	6.3	5.2	5.4	5.5
9. 1.80	5.3	4.7	5.5	5.1	5.3	4.8	6.3	6.1	4.5	6.0	6.0	5.8	6.5	6.6	6.6	6.6	6.0	6.7	6.5	6.5	5.3	5.6	5.4
30. 1.80	4.9	4.6	4.6	4.4	4.6	4.3	4.6	4.7	4.3	4.6	4.7	4.8	5.9	6.4	5.5	6.2	4.8	6.2	5.4	5.9	4.6	4.6	4.5
5. 3.80	5.6	4.6	5.5	5.3	5.2	4.7	5.9	5.9	4.4	5.6	5.7	4.8	5.9	6.1	6.0	6.1	5.8	6.2	6.1	6.2	4.9	5.0	5.0
2. 4.80	4.9	4.6	4.9	4.5	4.7	4.4	5.0	4.7	4.3	5.1	5.2	4.9	6.2	6.1	6.0	6.2	4.?	6.2	5.6	6.0	4.7	4.7	4.6
2. 5.80	6.5	-	6.5	6.5	6.3	6.0	6.6	6.7	4.7	6.1	6.2	5.2	6.6	6.7	6.6	6.5	6.6	6.7	6.8	6.6	6.0	6.2	6.2
4. 6.80	6.2	5.4	6.0	6.2	6.2	5.8	6.3	6.5	4.6	5.9	6.2	5.6	6.4	6.2	6.3	6.4	6.4	6.5	6.4	6.4	6.7	5.8	5.8
15. 7.80	6.7	5.6	6.3	6.5	6.6	6.0	6.6	6.7	4.7	6.3	6.6	5.8	6.6	6.8	6.6	6.7	6.7	6.8	6.8	6.6	5.3	6.2	6.1
6. 8.80	5.6	5.1	5.6	5.2	5.3	4.5	5.2	5.6	4.4	5.5	5.6	5.6	6.2	6.5	6.3	6.5	5.9	6.5	6.2	6.2	5.3	5.3	5.3
30.10.80	4.8	4.5	4.8	4.5	4.7	4.3	4.8	4.8	4.3	4.9	5.1	5.0	5.8	5.6	5.8	6.0	5.2	6.2	5.5	5.7	4.7	4.8	4.8
9.12.80	6.0	5.0	5.8	5.4	5.7	4.8	6.1	6.3	4.5	5.9	6.1	5.4	6.4	6.5	6.5	6.4	6.2	6.5	6.4	6.4	4.8	5.2	5.3
MEAN	5.7	4.9	5.6	5.4	5.5	5.0	5.8	5.8	4.5	5.6	5.8	5.4	6.3	6.4	6.2	6.4	5.9	6.5	6.2	6.3	5.3	5.3	5.3
STD DEV	0.7	0.4	0.6	0.8	0.7	0.7	0.7	0.8	0.2	0.5	0.6	0.4	0.3	0.3	0.4	0.2	0.6	0.2	0.5	0.3	0.7	0.6	0.6
STANDARD ERROR	0.2	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.2	0.2	0.2

pH

It was seen in Section 4.1.1 that the nitrogen concentration in streamflow is related strongly, though not in a simple manner, to discharge and other environmental conditions. The same phenomenon is present in the results of the spatial sampling, though the range of discharges sampled is restricted. The strong seasonal variation in nitrogen, specifically nitrate-nitrogen, concentration demonstrated for the outfalls of the main catchments in section 3.1 is mirrored

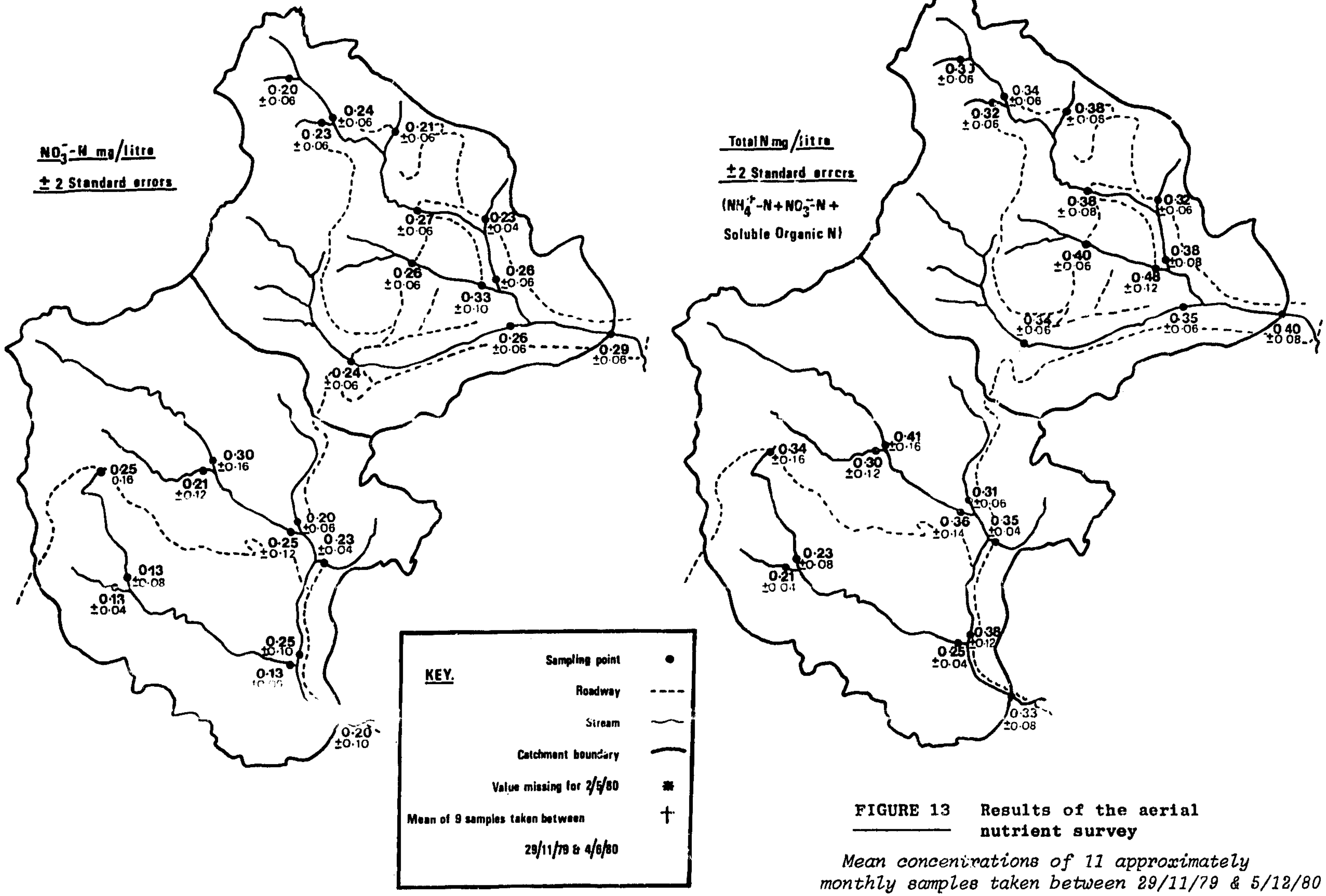
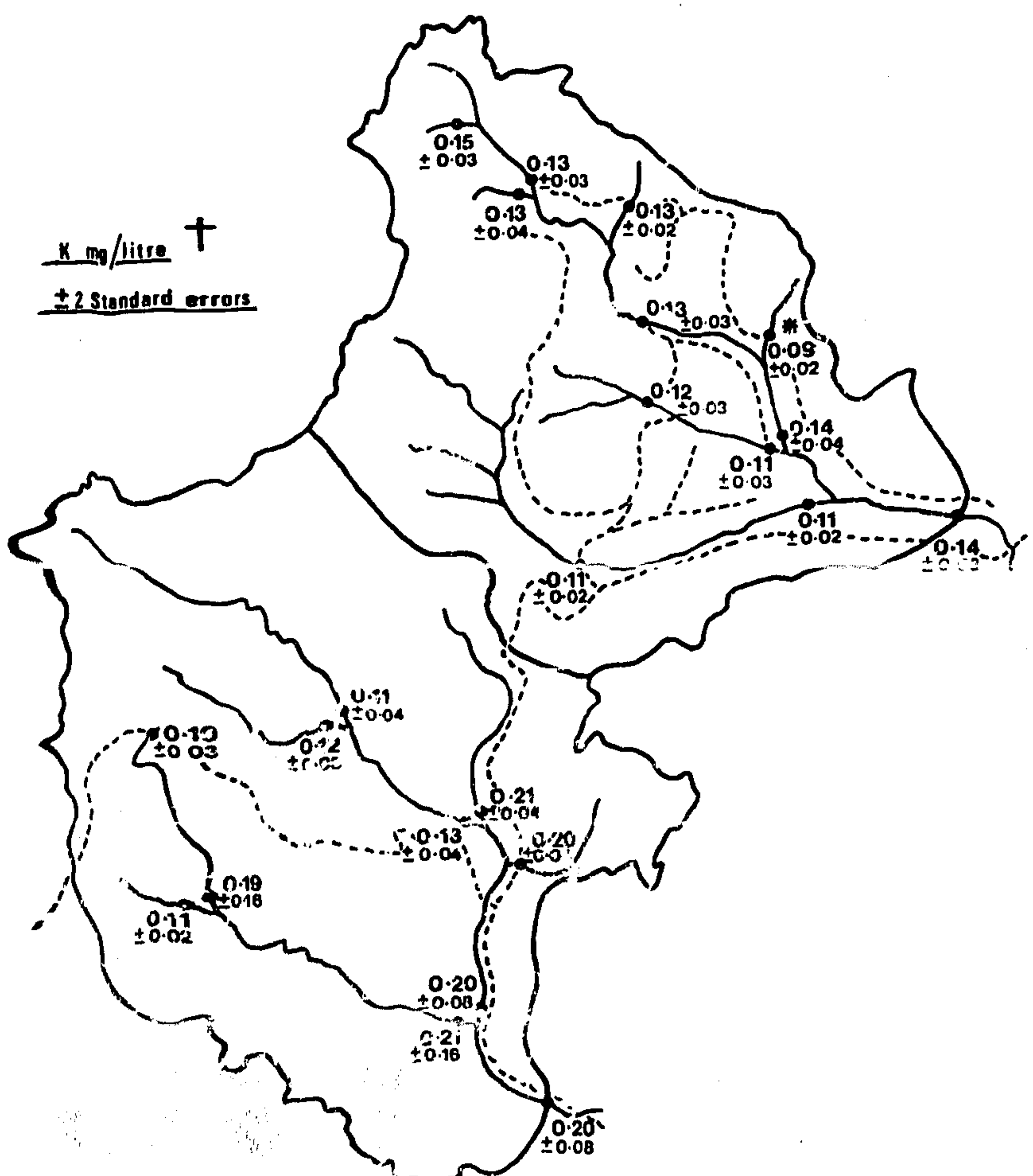
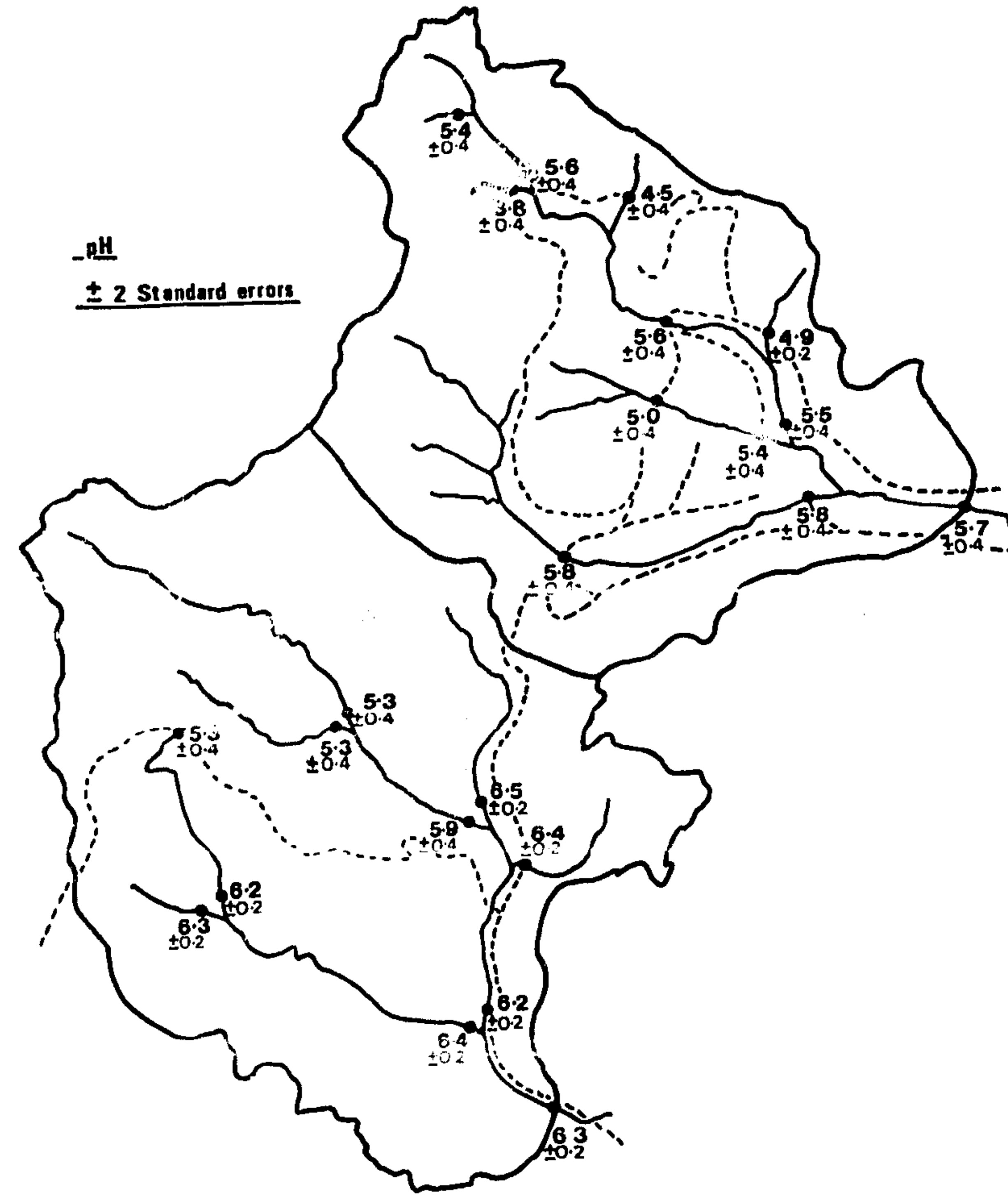


FIGURE 13 Results of the aerial nutrient survey

Mean concentrations of 11 approximately monthly samples taken between 29/11/79 & 5/12/80


K mg/litre †
± 2 Standard errors
0·15 ± 0·03
0·13 ±0·03
0·13 ±0·04
0·13 ±0·02
0·13 ±0·03
0·09 ±0·02
0·12 ±0·03
0·14 ±0·04
0·11 ±0·03
0·11 ±0·02
0·14
0·11 ±0·02
0·11 ±0·04
0·10 ±0·03
0·21 ±0·04
0·13 ±0·04
0·20
0·19 ±0·16
0·11 ±0·02
0·20 ±0·08
0·21 ±0·16
0·20 ±0·08


pH
± 2 Standard errors
5·4 ±0·4
5·6 ±0·4
3·8 ±0·4
4·5 ±0·4
5·6 ±0·4
4·9 ±0·2
5·0 ±0·4
5·5 ±0·4
5·4 ±0·4
5·8 ±0·4
5·7 ±0·4
5·8
5·3 ±0·4
5·3 ±0·4
6·5 ±0·2
5·9 ±0·4
6·4
6·2 ±0·2
6·3 ±0·2
6·2 ±0·2
6·4 ±0·2
6·3 ±0·2

by the time series of nutrient concentrations at various sampling points in the catchments (Fig. 15). The relationships between total nitrogen concentration and flow at the outfalls of each of the sub-catchments are shown in Fig. 14. For comparative purposes flow is "normalized" by being expressed in mm over the catchment. Although concentrations and flow were positively related in the main catchment monitoring results, the complex relationship indicated by the spatial survey (Fig. 14) suggests, as was expected, that the relationship is not causal.

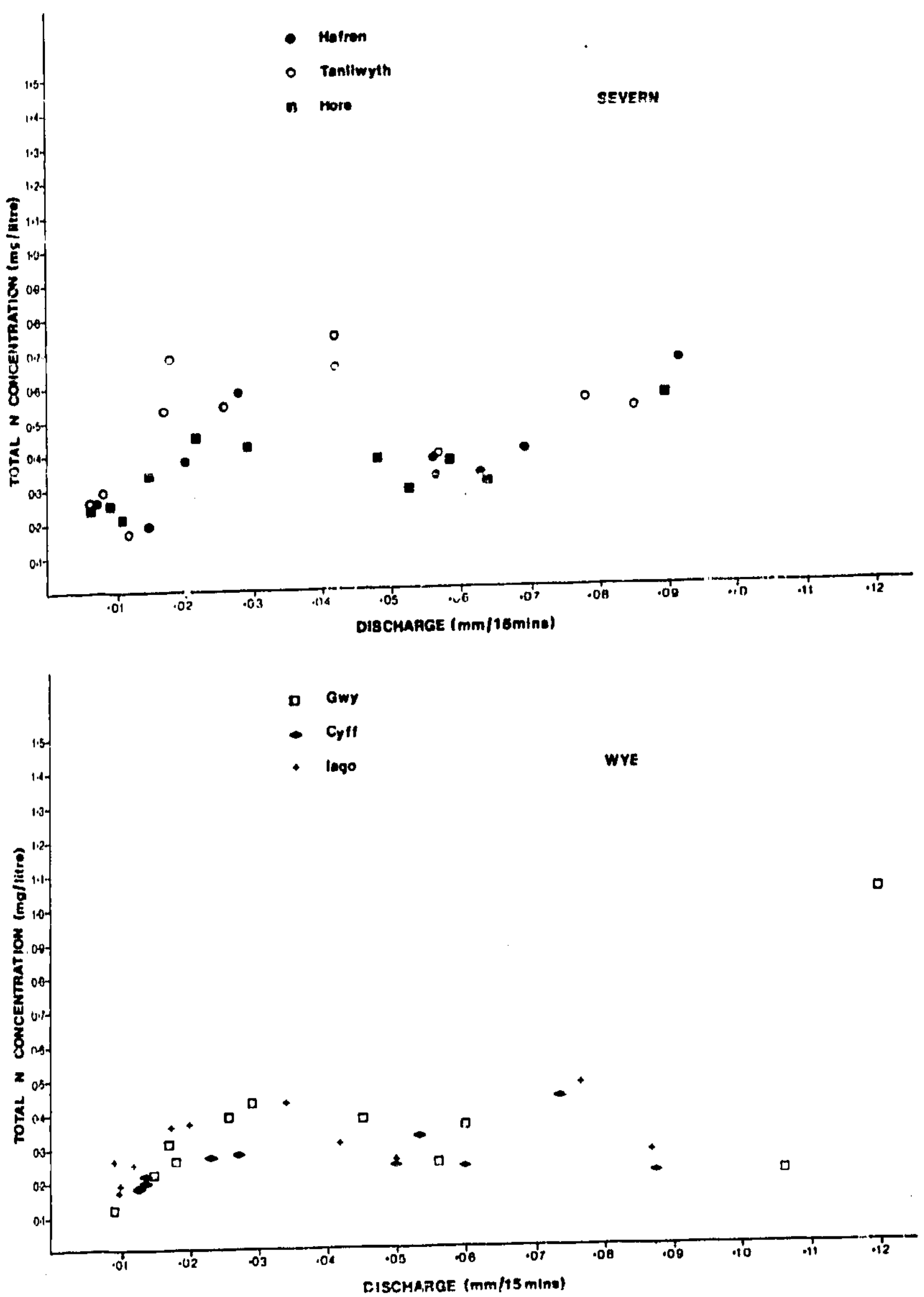


FIGURE 14 Relationships between total N concentrations and discharge for the sub-catchments

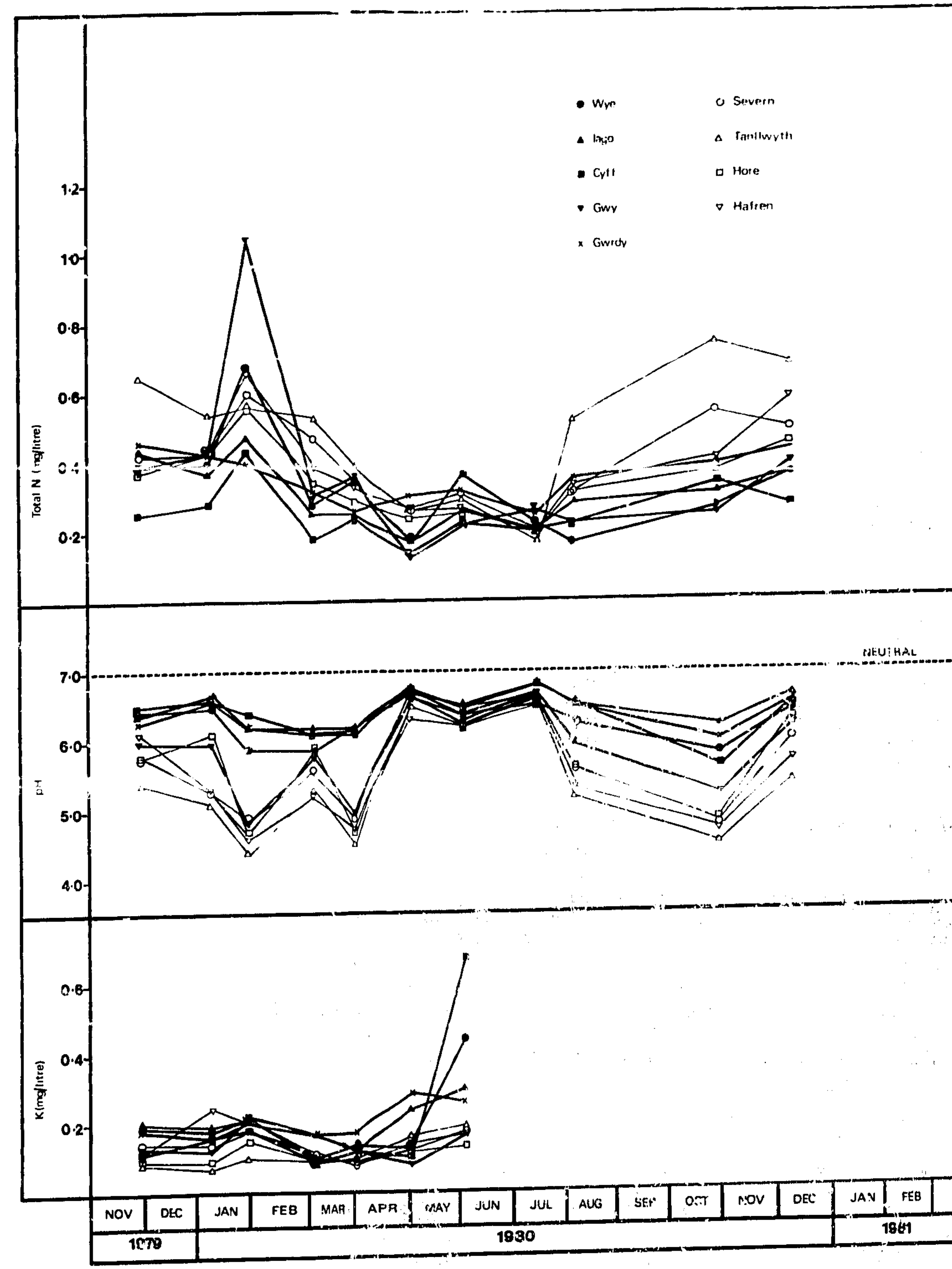


FIGURE 15 Time series of nutrient concentrations for the Wye and Severn and their independent subcatchments

At low flows (< 0.02 mm/15 min) a positive relationship is apparent for all the sub-catchments. At hi[illegible] flows [illegible] rapid rise in nitrogen concentration is apparent in the Gwy for only a small increase in flow. This is mirrored, albeit to a lesser extent, by the Hafren and Hore, though not by the Cyff, although all four catchments are of similar size and altitude range. No increase in nitrogen concentration with [illegible] observed at the outfalls of the two smaller sub-catchments, the [illegible] Iago. The high-concentration, high-flow relationship was obse[illegible] sampling time, namely 30.1.80, and the observed high nitrogen [illegible] would be due to the high proportion of [illegible] resulting from snow melt [illegible] that particular time. The results obtained in this study suggest (Fig. 16) [illegible] snow has higher concentrations of nitrogen than winter rainfall though the results obtained from other studies do not always support this observation (Herman and Gorham, 1957). Also, as snow lies for an appreciable amount of time, the nitrogen concentration rises even further by a combination of freeze-thaw weathering on bare soil areas and roadways and by the increase in the extraction of nitrogen under fr[illegible]zing conditions (T[illegible] et al, 1970) caused by the dehydration and increased permeability of biological membranes ([illegible], 1967). This argument would explain the absence of high concentrations in the Tanllwyth and the Iago as these are both lower altitude catchments in which the snow had already melted. It would also explain the higher nitrogen concentration in the Gwy compared to the Hore and the Hafren as snow does not tend to lie on the forest canopy and floor as long as on grassland. Also the Gwy has the most direct runoff pattern, uninterrupted and undamped in the way that the Hore and Iago are by mine workings and the Cyff is by the mesotrophic mires.

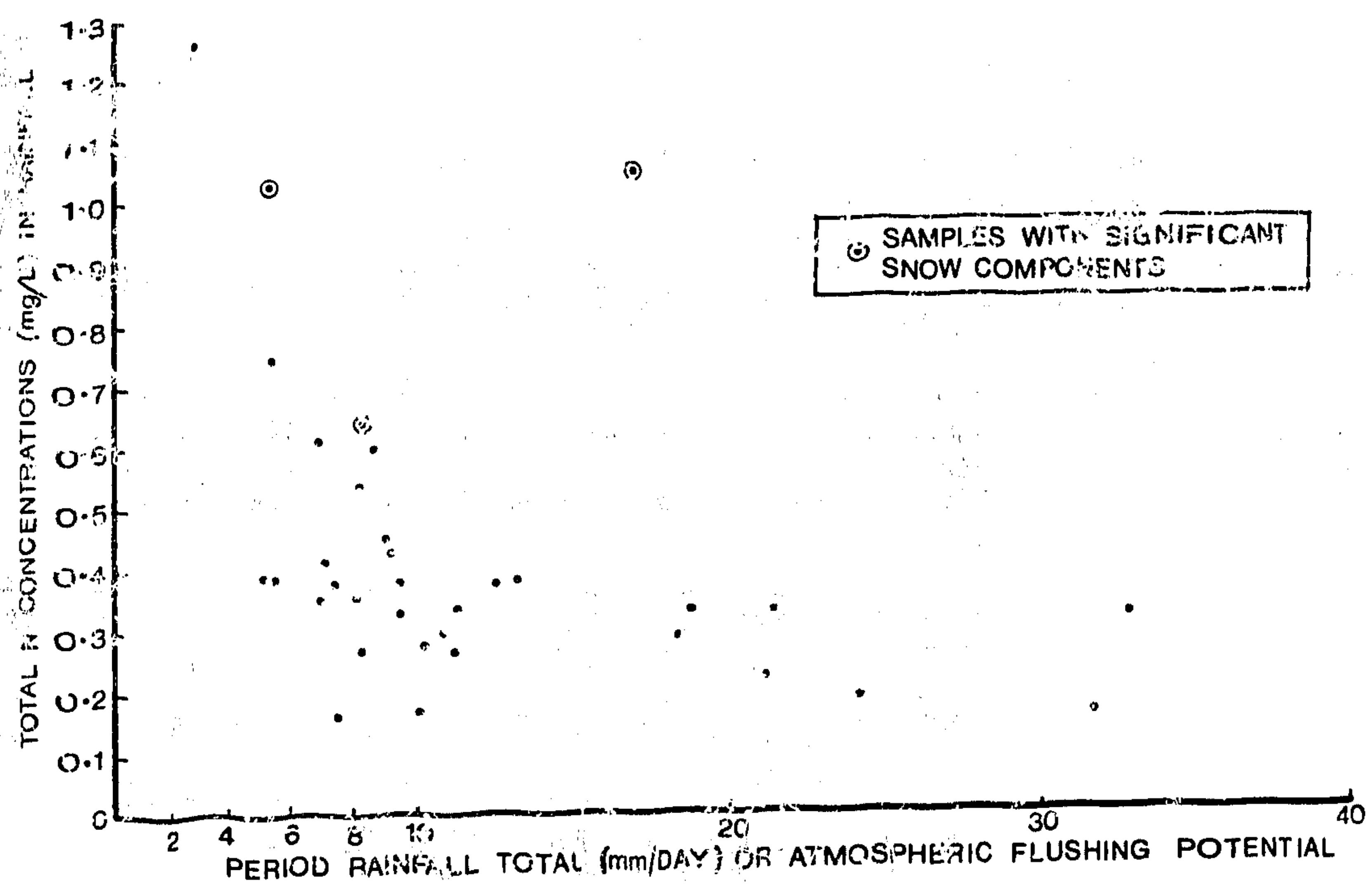


FIGURE 16 Total N concentrations in rainfall vs. period rainfall total

Although the overall relationship between nutrient concentrations and discharge is weak in these data (Fig. 14), there is some evidence of a nitrogen concentration peak occurring at discharge of between 0.02 and 0.[illegible] mm/15 min on the recession limb in both catchments; this is particularly evident in the Tanllwyth sub-catchment. From the mean concentrations shown in Table 6a, it is also obvious that the discharge of the Tanllwyth sub-catchment has consistently higher nitrogen concentrations than any of the other sub-catchments in the Wye and Severn. Inspection of Fig. 13 suggests also that these higher nitrogen concentrations are associated with processes occurring in the lower reaches. It is known that the Tanllwyth sub-catchment, a completely forested area, has a very active set of drainage ditches in its lower reaches that provide a source area for high rates of erosion and sediment transport. Rapid and efficient runoff has caused the deepening of these drainage ditches by the erosion of underlying boulder clay and transport of shattered scree material. Much of this is caught at the sediment trap at the outfall of the Tanllwyth sub-catchment; a study of the quantity of sediment collected showed four times the amount collected from a similarly sized grassland catchment, the Cyff (Painter et al, 1974). This erosion process also leads to the undercutting of the peat banks of the drainage ditches accompanied by drying out, bank collapse and transport of the organic products. However, not all of the nitrogen lost in this way is in the soluble organic form; much has been oxidised into the inorganic nitrate form. Here again the efficient drainage of the area is implicated, working by lowering the water table and promoting soil aeration. This upsets the natural mineralization/denitrification balance within the soil and allows nitrogen to escape freely to the stream, depleting the reserves of soil nitrogen in the process. There is, as a result, an export of nitrogen from the Tanllwyth sub-catchment that is not replenished by rainfall. This suggests that the soil system of the Tanllwyth sub-catchment is not in the state of chemical equilibrium that the grassland catchments and other forested catchments appear to be.

(c) Nutrient cycling within a coniferous forest

Results from the Plynlimon catchment experiment show a smaller water yield from the forested catchment, the Severn, than from the grassland catchment, the Wye (Calder and Newson, 1979). Process studies (Calder, 1976, and Gash et al, 1980), carried out in Plynlimon and elsewhere, have shown that the greater water loss from forested catchments is due to interception and subsequent evaporation of rainfall from the forested canopy. These studies have shown that up to 30% of the gross rainfall may be lost in this way, instantaneous losses depending on the wetness of the canopy and the rainfall rate. This water lost by evaporation from the forest canopy will be pure so the net result of the process is to reduce the volume of rainfall reaching the ground and to deposit in the canopy the nutrient content of the evaporated water.

Another source of nutrient input to forest ecosystems is by the trapping of air-borne dust particles in the tree canopy (Miller, 1979). The fate of the nutrients input in rainfall and introduced in air-borne dusts depends on the type of nutrient and time of the year. The nutrients are either retained in the forest canopy (foliar absorption), a process likely to be dominant during late summer or early winter, or leached down to the forest floor (Miller et al, 1976).

The bulk of the annual nutrient uptake in a closed-canopy forest is returned to the soil either in litter fall or crown leaching (Stenlid, 1958). Miller et al. (1976) in their study on Corsican pines, found that the greatest return of nutrients was in needles, the quantity of needle fall and their nutrient content varying throughout the year. It is likely, then, that the quantity and form of nutrients reaching the forest floor will vary throughout the year; this in turn will affect the nutrient concentrations in the streams.

With this in mind, a twelve month study was initiated in December 1979 within the Severn forest to measure and sample throughfall and stemflow for comparison with the gross rainfall. This was done using a 40 m^2 plastic sheet (Calder and Rosier, 1976), suspended beneath the canopy to catch the total throughfall and stemflow. The runoff from the plastic sheet was measured using a 1 litre tipping bucket discharge recorder (Edwards *et al*, 1974) connected to a MICRODATA event recorder. Flow proportional water samples were collected using an automatic sampler (Holdsworth and Roberts, 1982).

A summary of the results obtained is given in Table 7. This shows nutrient concentrations (mg/l) and loadings (kg/ha) in the gross rainfall, throughfall and stemflow for the periods during which reliable data were available. From the results obtained, it is apparent that, for the majority of the periods sampled, the total nitrogen concentrations in the throughfall and stemflow samples are less than those in the rainfall samples, whereas the reverse is true for potassium. This confirms the results obtained in other studies (Miller *et al*, 1976; Henderson *et al*, 1977). The results of the chemical analyses carried out on individual samples show a consistent decrease in the concentrations of the inorganic forms of nitrogen together with an increase in the concentration of organic nitrogen on passing through the canopy. This suggests the absorption of the inorganic forms of nitrogen by the forest canopy and an increase in organic nitrogen concentration either by the leaching of the forest canopy or from the pine needles accumulated in the plastic sheet (the plastic sheet was swept periodically but, nevertheless, pine needles did tend to accumulate upon it). Within individual storms, the increase in organic nitrogen was greatest during the early period of the storm. If nitrogen loadings are calculated (Table 7) then it is found that those in the throughfall are generally much less than those in the gross rainfall. Conversely, potassium inputs in throughfall are higher than those in rainfall.

TABLE 7 NUTRIENT CONCENTRATIONS (mg/l) AND LOADINGS (kg/ha) IN RAINFALL AND THROUGHFALL IN THE SEVERN CATCHMENT

	RAINFALL							THROUGHFALL						
	CONCENTRATIONS				LOADINGS			CONCENTRATIONS				LOADINGS		
PERIOD	TOTAL	N	P	K	N	P	K	TOTAL	N	P	K	N	P	K
20.12.79-3.1.80	116.3	0.42	0.01	0.15	0.40	0.01	0.17	103.4	0.28	0.02	0.60	0.29	0.02	0.61
30.1.80-7.2.80	151.6	0.42	0.01	0.06	0.64	0.02	0.09	131.4	0.30	0.02	0.44	0.39	0.03	0.58
7.2.80-15.2.80	75.7	0.18	0.01	0.05	0.14	0.01	0.04	63.3	0.21	0.01	0.05	0.13	0.01	0.03
15.2.80-19.2.80	19.6	1.29	-	-	0.25	-	-	13.0	0.33	0.01	0.10	0.04	0.00	0.01
19.2.80-3.3.80	42.6	1.41	0.01	0.08	0.60	0.00	0.03	28.7	0.56	0.02	1.10	0.16	0.01	0.32
5.3.80-13.3.80	96.0	0.24	0.01	0.04	0.23	0.01	0.01	76.6	0.40	0.01	1.22	0.31	0.01	0.94
19.6.80-24.6.80	45.0	0.48	-	-	0.22	-	-	58.3	0.26	-	-	0.16	-	-
26.6.80-1.7.80	48.3	0.59	-	-	0.28	-	-	31.3	0.38	-	-	0.12	-	-
6.8.80-20.8.80	111.3	1.34	-	-	1.49	-	-	82.1	0.62	-	-	0.51	-	-
29.8.80-10.9.80	54.9	1.28	-	-	0.70	-	-	47.4	0.40	-	-	0.19	-	-
10.9.80-24.9.80	106.9	2.10	-	-	2.24	-	-	73.0	0.76	-	-	0.55	-	-
24.9.80-8.10.80	150.8	0.33	-	-	0.50	-	-	130.4	0.39	-	-	0.47	-	-
22.10.80-29.10.80	137.9	0.14	-	-	0.19	-	-	97.2	0.35	-	-	0.34	-	-
11.11.80-26.11.80	323.5	0.15	-	-	0.48	-	-	180.0	0.35	-	-	0.66	-	-

4.1.3 Modifying influences to the general patterns of stream nutrient losses

(a) Variation over the flood hydrograph

An analysis of the chemical data from samples taken with the 'storm samplers' was undertaken in order to:

(i) Investigate changes in concentration of the various solutes over the storm period;

(ii) Calculate lag times to the peak or minimum concentrations of these solutes in order to better understand the mechanisms of solute transport.

On inspection of the data it became apparent that few of the storms sampled were suitable for the analysis of possible relationships between discharge and concentration because the chosen sampling interval was not suitable to approximate the shape of the concentration hydrograph. The problem arises because of the remote situation of the sampler, visited only once per week, and our inability when setting the sampler to foresee the intensity or duration of the next storm. The sampler operator can only guess at a convenient stage trigger level as this does not take a fixed value but must be varied dependent on antecedent conditions. Unless the site is visited frequently there is no opportunity to update continuously the stage trigger setting to take account of changing circumstances. Invariably much crucial information is missed, in particular details of concentrations on the rising limb of the hydrograph and peak solute concentrations; for long duration storms the limited number of samples (24) often means a loss of information on the recession limb also. In retrospect this would seem to be an ideal situation to have used a sampling controller such as the one described by O'Loughlin (1981) based on cumulative flow rates or the one by Martin and White (1982) based on rainfall rates or preferably one with a flow proportional microprocessor control.

On analysing the data from the suitable storms, it became clear that changes in nutrient concentrations do occur during storm events. an increase in discharge generally resulting in an increase in nutrient concentration. This confirms the findings of other studies (eg. Edwards, 1973; Walling and Foster, 1975). Fig. 4 shows the nutrient concentrations found in stream samples during two storm events; 15 min runoff is shown for comparison. The increase in concentration with increasing discharge was not consistent and was most pronounced during storms immediately following dry periods. The effect is not so apparent in winter when high flushing rates leach out any accumulated solutes.

Although the results obtained were rather variable, it has been possible to calculate the lag between peak discharge and peak solute concentrations for those storms that exhibit well defined peaks. This is shown in Table 8 where the times are in hours/mins, and the lag is defined as the time between peak discharge and solute peak (Heidel, 1956).

As indicated in Table 8 the results are rather variable suggesting that many factors influence the variation in solute concentrations in the stream discharge. However, there are some consistencies, as in the results for organic nitrogen. Here, two concentration peaks are usually obtained in the discharge of both the Wye and Severn catchments, one occurring at about the time of peak discharge and the other after a lag of between 1 and 4 hours. This would suggest two mechanisms for the transport of organic nitrogen to the streams, ie. direct surface runoff and as a result of soil erosion following heavy rainfall. This double peak effect is also found in the concentrations of the other nitrogen forms, ammonium-N and

TABLE 8 LAGS IN PEAK SOLUTE CONCENTRATIONS

Date	WYE Time of peak flow	Lag NH_4^+N	Lag NO_3^-N	Lag Org N	Lag P	Lag K	SEVERN Time of peak flow	Lag NH_4^+N	Lag NO_3^-N	Lag Org N	Lag P	Lag K
25.9.76	0400	+0100	-	0000 +0330	-	-	0300	-	+0230	-0030 +0230	+0100	-0030
14.10.76	1145	-	-	-0010 +0250	-	-	-230	-0030	-	+0430	+0430	-0030
23.10.76	0830	-0010 +0200	-	+0330	-	-						
6.12.76							0115	+0015	-	+0015	-	-
21.1.77							2045	+0330	-	+0130	-	-
10.2.77							1645	-	-	-0045 +0135	-	-
18.2.77	0030	-	-	-0115 +[illegible]45	-	-						
1.3.77	0930	-	+0030 +0300	+0300	-	-						
22.4.77							2230	-	-	+0045	-	-
1.9.77	2115	-	-	+0300	-	-	2030	-		+0345	-	-
[illegible].77	08[illegible] 1230	- -	- -	- -	- -	- -	0800	-0045 +0245	- -	-0030 +0245	- -	- -
30.9.77	2000	-	-0500		-	-	1930	-0330	-	-0300	-	-

nitrate-N. The transport mechanisms suggested for these two cases are (a) direct surface runoff, and (b) leaching through the soil profile.

Another interesting phenomenon observed is the occurrence of peak solute concentrations preceding peak discharges. This suggests either a peak concentration in the precipitation input in the earlier stages of the storms or that the bulk of the available solutes are transported to the stream very quickly, after which the supply becomes depleted. However, to test this hypothesis and the reason for the double solute peaks above, it would be necessary to sample many more storms, collecting and analysing surface runoff, and correlating stream solute concentrations with rainfall input and soil moisture status.

(b) Drought effects

The period under review is in many ways unrepresentative of the average conditions characteristic of the uplands of mid Wales. This limits our ability to generalise about the nutrient characteristic differences between the two land uses, especially if this information is used to predict possible effects of land use change. Nevertheless, the occurrence of severe drought conditions prior to (summer 1975) and at the start of (summer 1976) the study period and a relatively severe winter in 1978/79 tells us much about the processes involved in nutrient transport that would not be obvious during more tranquil times.

The main point of note in the data is the persistency of the drought effects. The low nitrate-N concentrations in the Wye streamflow characteristic of the summer of 1976 are seen to continue through winter 1976 and, if anything, are exacerbated in summer 1977. Concentrations in the Wye only recover to the Severn values in

January 1978. This highlights the fundamental point that the major control on nitrate-N concentrations in streams is nitrogen availability in the soil. Although flows returned to normal with a wetter than average autumn in 1976 concentrations did not, remaining low through the winter 1976/77. As the hydrological conditions during the winter 1976/77 were normal, the low concentrations in the Wye must have been caused by low mineralization rates, in themselves a produc[illegible] of low storage of organic N in the soil. This in turn was a function of low, stress-induced grassland produc[illegible]ivity in the summer 1976. That the Severn did not react in the same way is pr[illegible]y a result of the ability of larger plants to survive unusual environmental conditions by utilising their greater internal storage and root foraging capacities and, as indicated previously, the ability of the shallow aquifers to compensate for drought and spread the effect over a number of years.

The summer of 1977 also exhibits low values in the Wye catchment. This results from the low levels of soil organic nitrogen produced in the autumn and winter of 1976/77, though, following growth uninhibited by large soil moisture deficits in the summer of 1977, autumn dieback restores the balance to normal for the winter of 1977/78.

(c) Rain and snow distribution

Few of the differences in concentration in the streamflows [illegible] catchments can be attributed to vastly different rainfall o[illegible] catchments; the heavy convectional storm over the Severn in [illegible] the obvious exception (New[illegible] 1980). Fig. 17 indicates that the [illegible]

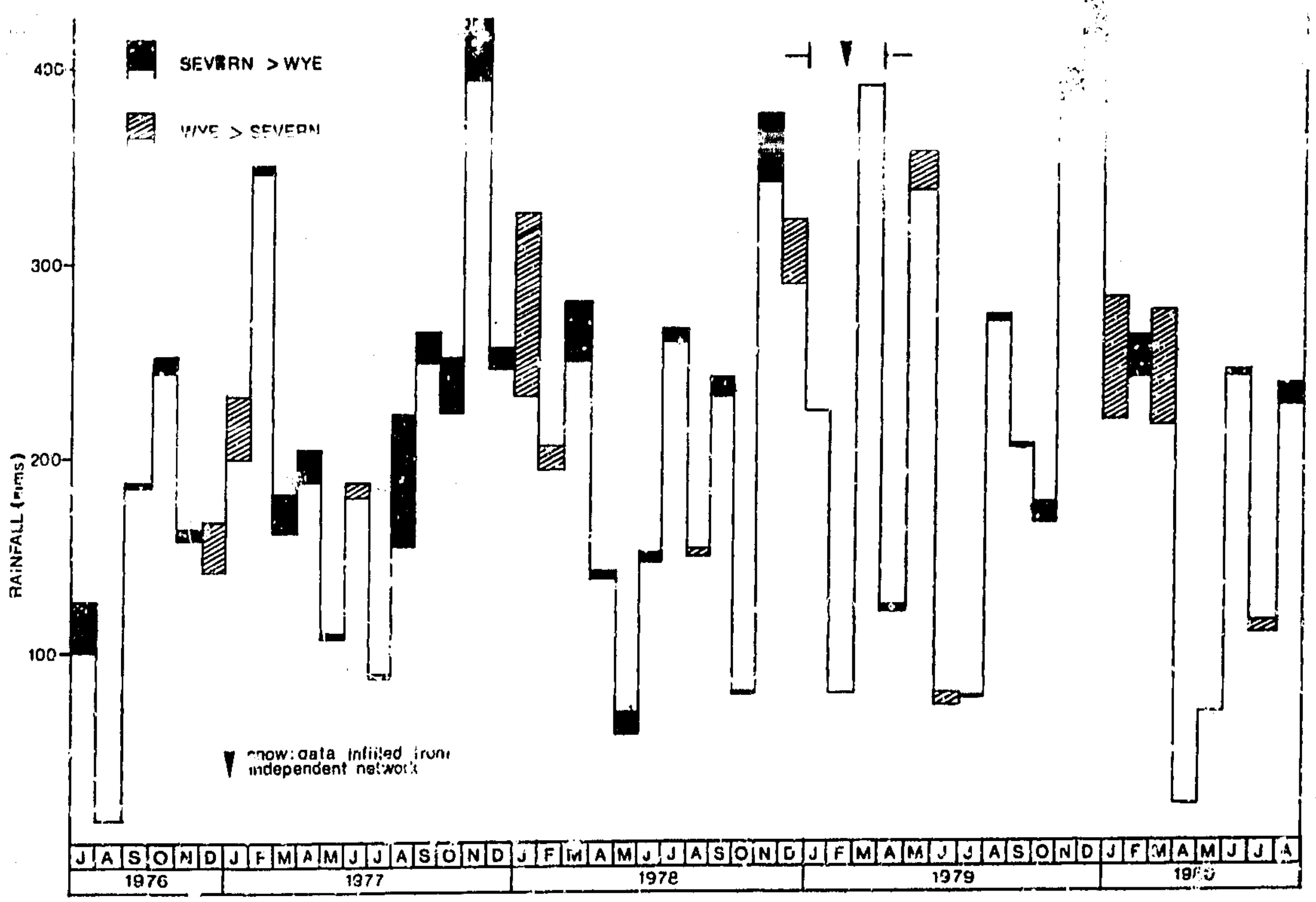


FIGURE 17 Comparative catchment rainfall totals for the study period

precipitation for the two catchments agree closely, to within 3.8% over the study period (1976-1980), while the long term (1971-1981) mean is even closer (< 2%). The discrepancy caused by poor raingauge performance in snowy weather (Clarke *et al*, 1973), however, can be serious and this is why data for the winter 1978/79, the worst since 1963, was replaced by data from a standard gauge network situated in the Severn catchment. Of necessity, rainfall for the Wye and Severn catchments are therefore taken as identical for January-March 1979 though in reality there were probably some differences. Problems arise with snow because as well as errors in the amount collected, the timing of input to the hydrological system can be delayed so that there is no immediate response from the stream concentration to the concentration in snowfall as measured in a raingauge. There is also some suggestion that snow is able to enhance its concentration while lying on the ground or in a raingauge funnel. This means that samples of snow taken by raingauge are fairly representative of the eventual input to the system provided the snow in the raingauge is not artificially melted.

It is apparent from Fig. 18 that there is no simple relationship between the nitrogen concentrations in the streams and those in individual rainfall samples during winter periods. No consistent trends for rainfall nitrogen concentrations appear for any of the three winters studied, in contrast to the obvious rising trends in the stream concentrations. If any common factor does exist it is represented by a mean winter total nitrogen concentration in rainfall of between 0.3 and 0.4 mg/l, much lower than the peak concentrations in streamflow.

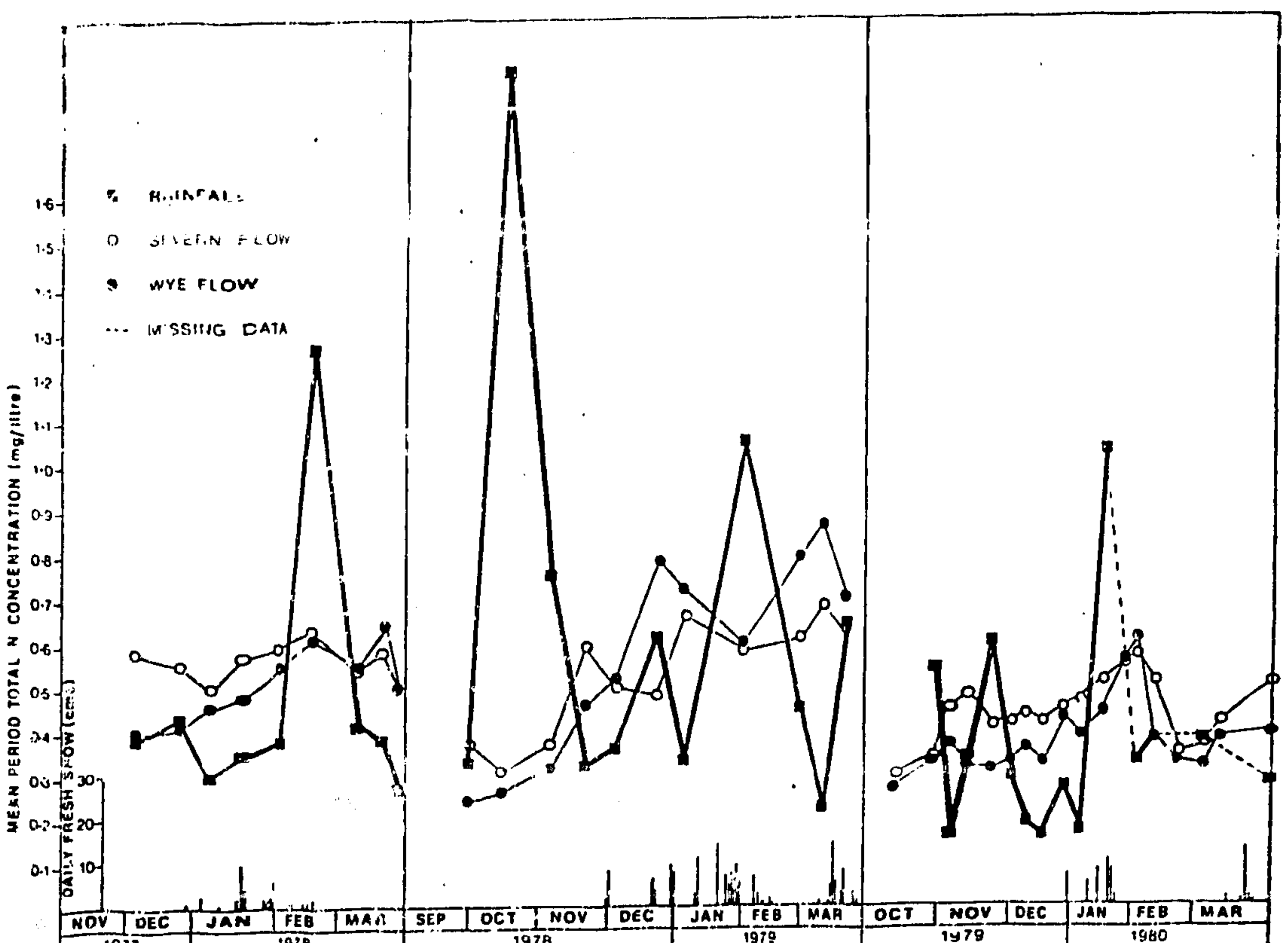


FIGURE 18 Winter total N concentrations in rainfall and flow

This generalization is modified, however, by high values in individual samples, most of which can be explained by the occurrence of snow in the sample. The largest deviations from the winter norms occur in February 1978, January-February 1979, and January 1980, all periods in which snow lay for longer than average. It is almost impossible to conclude from this whether snow has inherently higher concentrations of nitrogen than rainfall or whether the high concentrations are a function of concentration enhancement when lying. If enhancement is the cause, it is probably a function of dry deposition because freeze-thaw action in a copper raingauge funnel is not possible.

Other peaks are evident in Fig. 18 that cannot be explained by snowfall, including the largest of all, 1.91 mg/l of nitrogen, in October 1978. Concern was expressed at the outset of the experiment as to the need to preserve samples from biological deterioration. Apart from the concession of using brown sample bottles and the refridgeration of weekly cumulative samples if individual sample sizes were too small for analysis on their own, no other means of preservation, chemical or otherwise, was used. This was mainly because of the difficulty in maintaining a reasonable sample/preservative ratio. The effect of this can be seen in Fig. 19 where the length of incubation of the sample before analysis is positively related, if in envelope terms only, to the concentration of nitrogen in the sample.

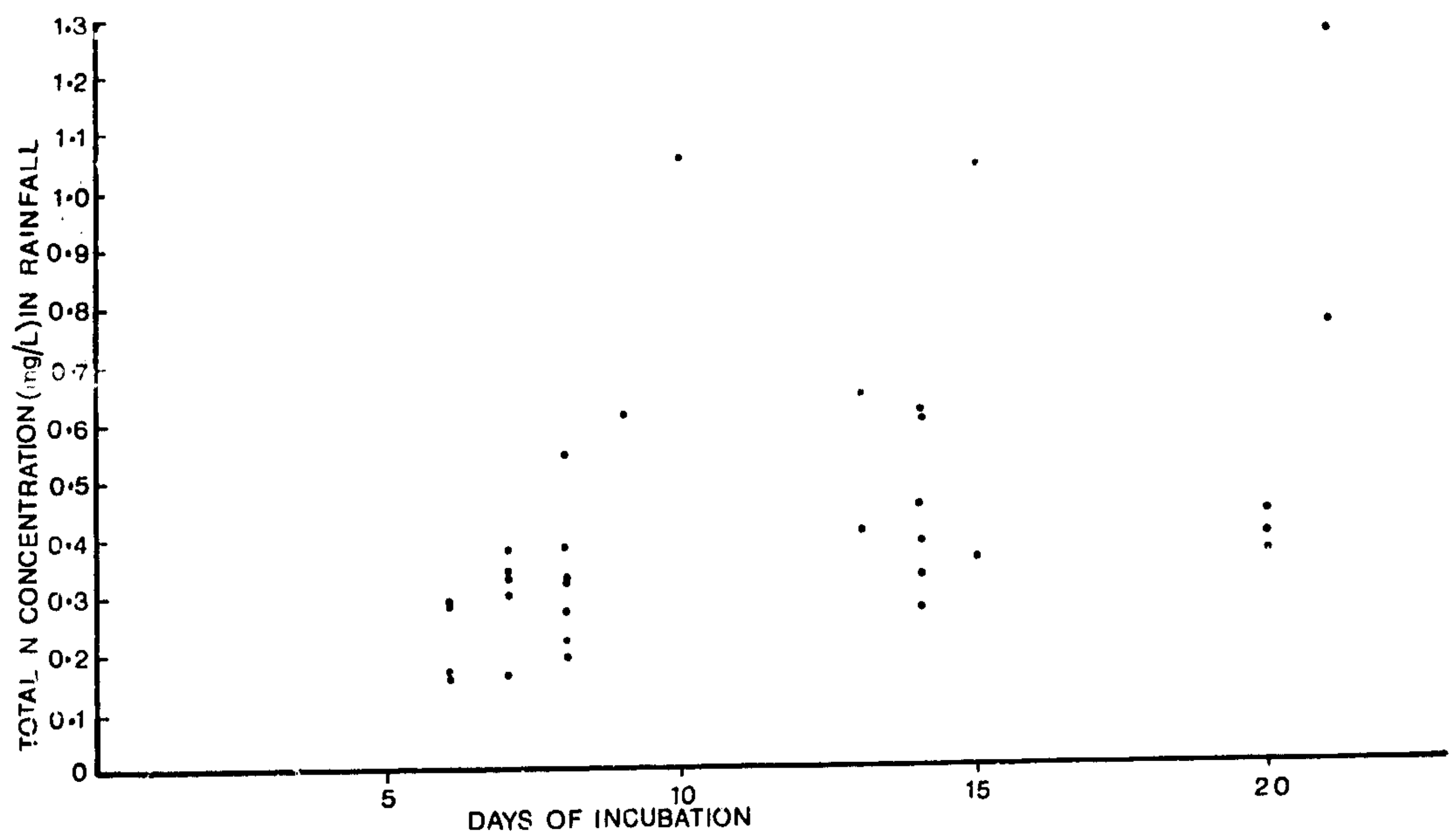


FIGURE 19 Graph of rainfall total N and length of incubation

This phenomenon may not be entirely causal, however, because as shown in Fig. 16, the length of incubation period is dependent also on the rainfall during that period. Another possible explanation of the trend in Fig. 19 is that during relatively dry periods, high nitrogen concentrations occur in the atmosphere - either in dust particles or in gaseous form. Conversely, at times of high rainfall (high atmospheric flushing potential), lower concentrations are common. The very steep increase in concentration evident at very low rainfall periods may also be a function of contamination caused by dust blown from dried out surfaces, increased movement of insect life and windblow of dead organic matter.

From Fig. 18 a possible reason for the low nutrient concentrations in streamflow during the winter of 1979/80 can be seen to be the lower than average rainfall nitrogen concentrations, in the range 0.14 - 0.3 mg/l, from November to January, the concentrations then reacting fairly strongly to snowfall in January (especially the Wye) and again in March when further snowfall occurred. The fact that the Wye tends to react more to snowfall than the Severn is probably indicative of the longer period of time that snow lies on the grass than in the forest canopy.

4.2 Comparative nutrient budgets for the Wye and Severn catchments

The use of the Wye (pasture) and Severn (forest) catchments for the long term water balance study and for this water quality monitoring exercise is based on the assumption that any differences observed will arise from the presence of coniferous forest on 70% of the Severn catchment. The geology, topography, soils, aspect and altitude range of the two catchments are similar, although there are some differences in the areal proportions of each feature. In particular, the organic heath peats renowned for their potential contribution to nutrient runoff by drying out (Terry, 1980) or erosion (Crisp, 1966) are more common in the Severn catchment than in the Wye.

For the water balance studies this assumption is justified by the identification of the forest canopy interception process as the major cause of the observed differences in streamflow volume. This difference in streamflow volume is a contributory factor to the differences in nutrient loadings between the catchments (Table 1), but it is difficult to determine, from the monitoring of the main catchment outfalls, whether the vegetation difference alone can account for the observed small differences in nutrient concentrations.

In the absence of continuous nutrient results from the subcatchments, differences in contribution from them cannot be properly quantified. Ideally it should be possible to define nutrient contributions from each soil/vegetation domain by the solution of simultaneous load versus areal extent equations for the subcatchments. However, with only data from the infrequent sampling of the spatial survey available, the results are meaningless for extrapolation purposes.

4.2.1 Extreme events

The significantly lower nitrogen concentrations in the Wye at the start of the monitoring period had effectively disappeared by late 1977, suggesting that this difference was triggered by the extreme drought conditions in 1976 rather than being an inherent long term effect of the vegetation difference. Similarly, as discussed in section 4.1.2(a), the higher concentrations in the Wye during some winter periods appear to be related to the longer duration of snow cover in this catchment. Thus differences are apparent in the catchment response to extreme events but in a way which relates only indirectly to the vegetation types.

4.2.2 Are the differences between the two catchments significant when compared to the within-catchment variations in nutrient levels

The within-catchment variations in nutrient concentrations from the admittedly sparse data obtained from the spatial survey (Fig. 13) emphasises the danger in attributing the catchment differences to vegetation alone. It can be seen that within catchment differences are at least as great as those between catchments. Examination of the mean total N concentration values indicates that the very low values in the Cyff sub-catchment of the Wye and the high values in the Tanllwyth sub-catchment of the Severn are the major factors determining the apparent

difference between means of 0.33 mg/l and 0.40 mg/l for the Wye and Severn main catchments. Without these contributions the means for the two main catchments would have been very similar. Indeed, had the Hafren and Gwy sub-catchments of the Severn and Wye been used for the forest versus grassland comparison, the annual means would have been almost identical at 0.38 and 0.36 mg/l, respectively.

The processes resulting in nitrogen enrichment in the Tanllwyth have been discussed in section 4.1.2(a). The contrasting process resulting in nitrogen depletion within the Cyff is considered to arise from the large proportion of valley bottom mesotrophic mire (Fig. 2) in this sub-catchment. These mires, with virtually permanent high water tables, through which water moves very slowly by a shunting process, are considered to act as nitrogen sinks in which denitrification by anaerobic bacteria occurs, particularly during periods of high temperature. Except in very wet periods, when direct overland flow occurs, hydraulic conductivity observations suggest that residence times in these mires could be of the order of months.

From these extreme cases, it would appear that soil and soil manipulation is at least as important in determining nitrogen concentrations as is vegetation type. If the role of the mires as nitrogen sinks is substantiated, their maintenance becomes an important factor in water quality control when intensive grassland improvement on the valley slopes is initiated.

The standard deviations of the annual means of nitrogen concentration give some indication of the seasonal variations. In the plot of standard deviation against mean N (Fig. 20), for all the sites in the spatial survey, there is an apparent positive correlation. This is less well defined for the independent sub-catchments.

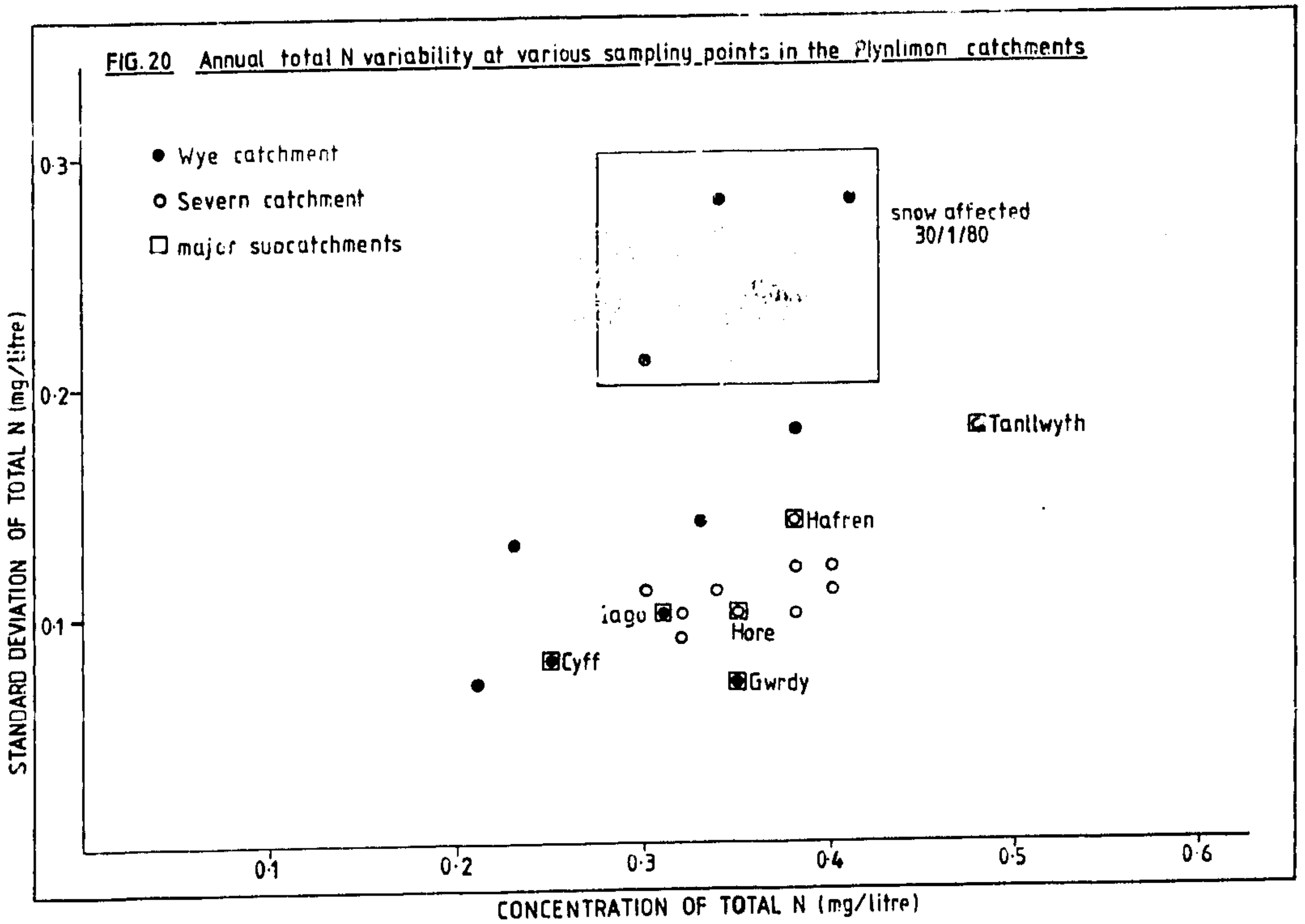


FIGURE 20 Annual total N variability at various sampling point in the Plynlimon catchments

Fig. 13 indicates that in the Wye high variability occurs in the Gwy sub-catchment and in the upper part of the Cyff but not in the lower Cyff, Iago or Gwrdy. In the Severn significantly greater variability occurs in the Tanllwyth. The damping effect of the mires in the lower Cyff and the enhancement processes in the Tanllwyth have been discussed above. It is possible that litterfall and decomposition in the grassland areas could account for the generally higher seasonal variations in grassland than in the forested areas. No obvious explanation can be advanced for the low variabilities in the Gwrdy and Iago sub-catchments other than to comment [illegible] a large proportion of the flow from each moves through old abandoned mine workings, which may help to damp any seasonal variation.

Phosphorus concentrations were at or below the detection levels employed in the chemical analyser (0.02 mg/l) in this study so little can be deduced about their spatial variations. Potassium, however, was found to vary in an interesting fashion. Between-site differences were small in the Severn with marginally higher concentrations in the eroded peat hag areas of the upper Hafren. It was shown in section 4.1.2(b) (Table 7) that potassium concentration in forest throughfall is generally greater than in the rainfall. The fact that this enhancement in potassium concentrations is not evident in the streamflow is a comment on the efficient absorption of this ion by the forest soils. Spatial variation in potassium concentration in the Wye was found to be much greater than in the Severn, with a distinct split between sites in the 0.10 - 0.13 mg/l range and those in the 0.19 - 0.21 mg/l range. Comparison of Figs 13 and 2 indicate that the former occur at points draining relatively unimproved hill land (H2 - H4 on the MAFF (ADAS) Hills and Upland Classification) whilst the latter occur at points where a high proportion of the drainage is from reseeded areas which receive periodic applications of basic slag (U3S on the MAFF scale). A similar pattern is evident in the spatial variation of the pH values in the Wye, with the higher values coinciding with drainage from 'improved' areas.

Whilst these high pH values in the 'improved' areas of the Wye are higher than those in the Severn, it is interesting to note that the Severn pH values are not significantly lower than those in the 'unimproved' areas of the Wye. This may well arise from the fact that most of the streams are incised into the relatively base-rich underlying drift and boulder clay. In a detailed study of grassland improvement effects at a site in the Wye catchment (IH, 1980) it was found that cutting through the peat into the underlying bounder clay resulted in an increase in the pH of the drainage water.

4.2.3 The implication for water quality of land use change to forestry

From the arguments explored it is clear that no significant long-term differences in terms of average nutrient concentrations in the discharges of the Wye and Severn catchments can be attributed solely to the coniferous forest and forest management in the Severn. Though differences exist, they can generally be explained by other internal peculiarities of the two catchments particularly during extreme events. One exception to this is lying snow which, because of its tendency to remain on grassland areas for longer than on the forest areas, is able to increase its nutrient content by freeze-thaw action and its effects on biological membranes. By their very nature, however, extreme events such as these are infrequent and in terms of the effect on total nutrient loadings, of little consequence. The same can be said of drought effects and although large soil moisture deficits under forest areas do have an effect in reducing summer concentrations, of nitrogen at least, in the stream water, the quantification of this with the data at our disposal is difficult because of the compensatory effect of hydrological storage in the Severn catchment.

In order [illegible] the effects of forest on nutrient runoff, much more information [illegible] nutrient cycling within the vegetation/soil systems of the Wye [illegible] concurrently with continued sampling at the catchment outfalls [illegible] discussion of the processes [illegible] work, the inputs and outputs of nutrients [illegible] in balance in both the [illegible]ed and grassland catchments at present, [illegible] possible exception of the Tanllwyth sub-catchment of the Severn where [illegible]osion is resulting in some net output. This balance is a delicate one however. [illegible] decrease in the buffering effects of the shallow aquifers or mires through channel modification, or large scale soil disturbances with its erosion and oxidation effects could lead to considerable increases in stream concentrations unless balancing factors are also introduced.

Whilst such potential increases in concentration may seem insignificant relative to those encountered in lowland river systems, the reduction in the downstream dilution effectiveness is the major factor to be borne in mind. This is particularly important in considering the effects of afforestation where there is the additional effect of the reduction in streamflow volume by up to 20%.

5 CONCLUSIONS

The main results obtained during the course of this study and the suggested explanations for the trends found are as follows:

(i) There is a seasonal variation in nitrate-N concentration in both streams - low in summer and high in winter. This was thought to be due to the growth cycle and dieback of plants. In the growing season any nutrient-rich rainfall is rapidly used by soil micro-organisms and plants before it can contribute to the streamflow, whilst in the winter, the nitrogen concentration in the rainfall is enhanced by the nitrogen formed by the mineralization of decayed plant residues. Winter peak nitrate-N concentrations in the streams coincide with the maximum amount of available organic nitrogen in the soil. The differences in the peak winter concentrations from year to year are thought to be due to the percentage of precipitation input occurring as snow.

(ii) Higher nitrate-N concentrations were found in the stream draining the forested catchment especially during 1976 and 1977. Two further studies were initiated to try to explain this difference. Throughfall samples were collected below the forest canopy and an areal sampling survey made of both catchments. The results of these studies suggest that the differences were due not to canopy enrichment of the rainfall but more to a land management and hydrogeological effect. The valley bottom mires in the Wye catchment, because of their high water tables and the time taken for water to permeate through them, act as nitrogen sinks by losing the gaseous forms of nitrogen by denitrification. This is especially so in periods of high temperature as experienced in 1976. The mires that existed in the Severn catchment, however, have been drained to aid sapling development and these drains provide a rapid route to the stream for any nutrient-rich rainfall. Also, the more extensive shallow aquifers and drift deposits in the Severn catchment hold up its water yield more effectively than the Wye catchment. The provision of these extra stores helps to damp year-to-year variations in the pattern of both water and nitrogen runoff and results in the Severn catchment being less-susceptible, in quantity and quality terms, to desiccation by drought. The fact that the depression of the nitrate-N concentrations in the discharge of the Wye catchment was extended well into 1977 was due to the knock-on effect of the low, stress-induced, grassland productivity during 1976 and the subsequent low quantities of organic nitrogen made available for mineralization during the winter 1976/77. That this did not happen in the Severn catchment is a reflection of the greater foraging capacity of the roots of the spruce trees.

(iii) In terms of nutrient losses, the larger flows from the grassland catchment compensate for the lower nitrogen concentrations. A comparison of nutrient inputs and outputs in rainfall and runoff from both catchments showed a net input of nutrients in the months April to October and a net output in November to March. An annual nutrient balance showed a net input of 10 kg/ha of nitrogen and parity for potassium and phosphorus.

6 DISCUSSION

The data obtained during the course of this and other studies carried out in the upland areas of Britain give an insight into the processes occurring in these areas. More importantly, however, they highlight the deficiencies in our data collection techniques and the gaps that still exist in our knowledge of these processes. It may be instructive, therefore, to review the progress made in our understanding of nutrient cycling in upland Britain and to suggest ways of improving existing techniques.

6.1 Review of present study

This study began purely as a monitoring exercise to determine the nutrient concentrations in the grassland, Wye, and the forested, Severn, catchments. The data obtained could then be used, in conjunction with the hydrological data collected from the two catchments, to calculate the quantities of nutrients discharged from the two land uses. In addition, the data would prove invaluable as background levels to future studies into the effects of land use changes - grassland improvement and the forestry practices of planting, fertilizer applications and clear felling - on water quality. For these two purposes the data collected proved to be perfectly adequate but, as the study progressed, additional samples were collected and analysed to try to explain the variations and differences in the stream nutrient levels and to calculate nutrient balances for the two catchments. It was at this stage that the limitations of the data collected became apparent.

6.1.1 Data collection techniques

Basically, two types of water samples were collected - streamflow samples to compare nutrient concentrations in the discharge of the two catchments and at various points in the two catchments, and rainfall samples to calculate inputs to the catchments for nutrient balance purposes. In general, the results obtained from the analysis of the streamflow samples proved to be more satisfactory than those from the rainfall samples. Opinions vary as to whether the results obtained from the analysis of rainfall samples filtered in the funnel as they are collected give a more accurate estimate of nutrient input than do unfiltered samples. For filtered samples, any dry deposition caught in the filter will be leached by successive rainfall input. Normally these filters are renewed when the sample is collected and it may well be that, in consequence, this debris will not be fully leached. In unfiltered samples, however, this debris, provided that it is not too big, passes through the funnel into the sample container where it is leached continuously by the sample. This would seem to be a better approximation of what is input to the catchment as a whole as any dry deposition on the ground surface will be broken down eventually into soluble nutrients, the only difference being the greater time taken for the debris on the ground surface to be leached. However, it is inevitable that debris, both plant and animal, will accumulate in greater quantities in rain collector funnels than on the ground surface and this will cause overestimation in nutrient input and areal variations. The results of the comparisons between the rain collectors in the Wye and Severn show that, in general, the inputs agree quite closely but that for certain periods, especially during the summer months, large differences do exist. These must be caused by different quantities of dry deposition being trapped in the two collectors. It would seem, therefore, that filtered rainfall samples underestimate nutrient inputs whilst unfiltered samples overestimate, particularly during the summer months. It would be instructive to compare the results obtained from filtered, permanent and renewed, and unfiltered samples at the same location, analysed at the same laboratory using the same techniques. This would at least quantify any discrepancies in the two techniques.

Another problem associated with collecting rainfall samples for analysis is the time lapse between the occurrence of rainfall and the analysis of the sample. During this time many transformations, particularly between the various nitrogen species, may occur and the results of the analyses may not bear any resemblance to those that would have been obtained when the rain fell. It is unlikely, though, that any great change will have occurred in the result obtained for total nitrogen. There are two possible solutions to this problem; analysing rainfall as soon as it falls, an impossibility in remote upland stations, or adding a preservative. The problem with the second alternative is that of maintaining the correct sample/preservative ratio. It is probable that the transformations occurring during the big changes in sample/preservative ratio as a result of adding a certain quantity of preservative at the beginning of the sampling period may well be greater than those occurring in the absence of any preservative. The only solution is to devise some means of adding the preservative at a comparable rate to the rainfall. An approximation to this can be obtained by using an event recorder type of raingauge such as the tipping bucket or the Dines syphoning recorder and adding the appropriate quantity of preservative for every tip or syphon.

The sampling techniques used for monitoring the discharges of the two catchments, ie. daily values obtained from the analysis of a bulked sample comprising three eight-hourly spot samples, was satisfactory for comparing the nutrient concentrations in the two streams and for looking at seasonal variations. They were less than satisfactory for comparing nutrient concentrations with other hydrological variables and for the calculation of nutrient balances. For the former, spot streamflow samples would be required together with instantaneous measurements of the other variable(s). This is especially so in areas such as Plynlimon where conditions change rapidly. The results of the "storm" sampling, although much more suitable for comparison with other variables, were not ideal. Apart from the problems indicated in 4.2.3(a), they were not obtained from the analysis of spot samples. For nutrient balance purposes, a more accurate estimate of nutrient losses in streamflows would have been obtained by the collection of composite samples, preferably on a flow proportional basis. In common with the rainfall samples, those from the streams were unfiltered and unpreserved although, in this case, studies into the effects of different time lags between sample collection and analysis showed little or no changes in nutrient concentrations.

In spite of the reservations felt about the data collected during the course of the study, a detailed analysis was carried out to try to explain the variation and differences in the data from the two streams and to speculate on the factors affecting nutrient release into upland streams. A number of suggestions were made though not tested and it would be interesting to carry out further work to determine whether in fact these suggestions were valid.

6.1.2 *Supplementary data required*

The seasonal variation in nitrate-N concentrations found in the discharges of both the Wye and the Severn catchments was explained in terms of the growth and decay cycle of plants. During the growing season (April to September) the available nutrients in the upper layers of the soil are utilized by micro-organisms and plant growth before they can be leached beyond the rooting zone and contribute to the nutrient concentrations in the streams. During the dieback period (October to March) plant material is returned to the soil system as litterfall. This is gradually broken down by micro-organisms resulting in a build-up of soluble nitrogen in the soil, the maximum amount occurring during January or February corresponding with maximum nitrate-N concentrations in the streams. In order to verify this and to relate input in rainfall and outputs in the streamflows it would be necessary to collect foliar samples during the growing seasons and samples of litterfall during the dieback period to ascertain the quantities involved in the internal nutrient cycle. Also, it would be necessary to collect soil and soil water samples together with soil moisture [illegible] ings to ascertain the concentrations and quantities of soil moisture availab[illegible] hing into the streams. Using this information it would also be po[illegible] ate mineralization rates and to relate them to available organic ma[illegible] oil temperature, soil moisture and pH. Clearly this would be a considerable ta[illegible] volving the collection and analysis of many samples of soil, soil solution, [illegible] ge and litterfall to obtain a reasonable representation of the required data; these have been shown in the past to vary considerably over relatively small areas.

Another possible contributory factor to peak nitrate-N concentrations in the streamflows during the winter is the occurrence of precipitation in the form of snow; it cannot be just a coincidence that the maximum values occur during those periods which contained the great[illegible] number of days when snow lay on the ground. Whether snow has inherently higher concentrations of nitrogen than rain or whether it becomes contaminated whilst lying on the ground is unclear but would be a relatively simple matter to determine.

The cause of the variation in stream nutrient concentrations over a storm period could be studied by the continuous monitoring of rainfall, surface, sub-surface and streamflow, extracting soil and soil water samples and measuring water levels in [illegible], or taking soil moisture readings before, during and after the storm

appropriate to carry out this study at a number of small plots representing different areas of the catchments.

Two possible reasons were put forward for the depression of the nitrate-N concentrations in the discharge of the Wye catchment during the summer 1975. The mesotrophic mires, present in the Wye catchment but destroyed by pre-planting drainage in the Severn, contribute much to the Wye streamflow during dry periods. However, water movement through these mires is so slow that during hot periods they act as nitrogen sinks by providing ideal conditions for the gaseous loss of nitrogen by denitrification. Thus the water emerging from these mires is nitrogen depleted causing low nitrate-N concentrations in the Wye catchment during drought periods. In contrast, the drainage lines present in the Severn catchment provide a rapid route to the main stream for water from the head of the catchment without appreciable loss of nitrogen by denitrification. Alternatively, the shallow aquifers and drift deposits in the Severn catchment hold up the water yield more effectively than in the Wye catchment. These extra stores help to damp year-to-year variations in the pattern of both water and nitrogen runoff and results in the Severn catchment being less susceptible, in quantity and quality terms, to desiccation by drought. These alternatives could be investigated by an extension of the areal sampling programme and using the results of the chemical analyses, together with flow records, to formulate simultaneous equations relating concentrations and loadings to differing vegetation and soil types within the sub-catchments; from the [illegible] relationships, characteristic concentrations and loadings from the various land types can be calculated and used, with suitable areal weightings, to predict nutrient levels and loadings in similar ungauged catchments. Also, any gaseous loss from the mesotrophic mires and other areas could be monitored by collecting soil and soil water samples and by collecting and analysing air samples (Dowdell and Webster, 1976).

6.2 Nutrient cycling in upland Britain

It is obvious from the preceeding section that much work remains to be done before an understanding of the factors involved in nutrient release in the uplands is realised. Ironically, many studies have been carried out but rarely in the same environment and at the same time. However, it may be instructive to describe briefly some of those studies relevant to the uplands of Britain.

6.2.1 *Review of past and present studies*

Over the last century many aspects of upland ecosystem nutrient cycling have been researched but it is rare for a multidisciplinary approach to the modelling of the systems to have been adopted or even for the many independent studies to have occurred simultaneously on the same catchment. The lack of cross-referencing implicit in the latter statement is true for the Plynlimon experiment where, at some time or another, nutrient inputs in precipitation have been studied by Roberts and James (1972), Cryer (1976) and the present authors, the first two studies excluding nitrogen and phosphorus. The AERE Harwell have also been responsible for continuous monitoring at Plynlimon of most of the nutrients in rainfall.

Vegetation sampling for production studies have been undertaken by [illegible] b and Taylor (1978) but, unfortunately, not for the same period as the present study and not in terms of nutrient utilization. Studies of nutrient cycling in grassland areas (Floate, 1970) and forests (Miller et al, 1976) have proved useful in qualitative terms but because of geographical and botanical disparities, the results cannot be extrapolated quantitatively to Plynlimon.

Aspects of soil biochemistry, crucial to the understanding of the processes of nutrient movement, have not been extensively researched in the uplands of Britain and ideas for the effects of mineralization and denitrification rely upon laboratory incubation experiments from the USA (Stanford and Smith, 1976; Kanwar et al, 1982). Field measurements of these and also of nitrogen fixation are notoriously difficult but must be attempted to understand the processes involved. Much of the quantitative information regarding these processes comes from nutrient balance attempts. Crisp (1966) is probably the best example for upland Britain with Cryer (1980) carrying out a similar study on the Maesnant catchment to the northwest of Plynlimon, but dealing with nutrients other than nitrogen and phosphorus.

It is in the area of nutrient movement and its relationship with hydrology that the work reported has made major steps forward. Although Roberts and James (1972) sampled river water for comparison with rainfall at Plynlimon, the detail of concentrations and flow variation is inadequate for discussion of causal relationships. Osborne et al. (1980) using data from the Harmonized Monitoring Scheme have attempted to isolate land use effects in large catchment tributaries of the River Wye but did not specifically study the upland case. The most comprehensive study is probably that of Crisp (1966) whose inclusion of many of the factors involved in upland nutrient balances was commendable (organism drift in streams, peat erosion by sampling particulate organic matter in streams, net loss by agricultural productivity) as was his approach covering the whole spectrum of nutrients. The limitations of his study were mainly technological - the lack of temporal flexibility in his river sampling methods, the lack of spatial validity in his rainfall estimates and the absence of any attempts at quantifying soil processes for explanatory purposes. To some extent the same criticisms can be levelled at this study but at least some attempts have been made to improve the rate of sampling from the river system and to achieve some replication of rainfall samples.

6.2.2 Future work

Studies into the effects of upland land use changes on water quality, the natural extension to this present study, are already underway within the Natural Environment Research Council and other associated establishments. The table below summarizes the studies, their location and establishments involved.

In addition, the Freshwater Biological Association are studying the effects of different land uses on aquatic life, particularly fish populations, though not in any of the locations mentioned above.

The effects of the land use changes are studied by a comparison between a control and an experimental site with a period of inter-comparison between the sites prior to the land use changes. If feasible, the studies are carried out on a catchment and a small plot scale. In this way, an overall appreciation of the effects of the land use changes plus an insight into the reasons behind and the processes involved in the effects may be gained.

Location	Land use change	Scale of study	Start	End	Establishment
Plynlimon	Grassland Improvement	Plot	1977	1981	IH
Plynlimon or HFRO Sourhope	Grassland Improvement	Catchment	1983	-	IH
Llanbrynmair	Afforestation	Catchment	1982	-	IH
		Plot	1982	-	UCW
Glen Orchy Scotland	Remedial Fertilizer Application to Forestry	Catchment	1981	-	WRC
Beddgelert Wales	Clear Felling	Plot	1981	-	ITE
Kershope Northumberland	Clear Felling	Plot	1981	-	ITE
Plynlimon	Clear Felling	Catchment	1983	-	IH
		Plot	1983	-	ITE

Key to Establishments

IH Institute of Hydrology
UCW University College of Wales, Aberystwyth
Department of Geography
WRC Water Research Centre, Medmenham
ITE Institute of Terrestrial Ecology

REFERENCES

Ångström, Anders and Högber, Linus (1952). On the content of nitrogen (NH_4-N and NO_3-N) in atmospheric precipitation. *Tellus*, 4(1), 31-42.

Ångström, Anders and Högberg, Linus (1952). On the content of nitrogen in atmospheric precipitation in Sweden. II. *Tellus*, 4(4), 271-279.

Batey, T. (1982). Nitrogen cycling in upland pastures of the UK. *Phil. Trans. R. Soc. Lond.*, B 296, 551-556.

Calder, I. R. (1976). The measurement of water losses from a forested area using a "natural" lysimeter. *J. Hydrol.*, 30, [illegible]-325.

Calder, I. R. and Rosier, P. T. W. (1976). The design of large plastic-sheet net-rainfall gauges. *J. Hydrol.*, 30, 403-405.

Calder, I. R. and Newson, M. D. (1979). Land-use and upland water resources in Britain - a strategic look. *Water Res. Bull.*, 15(6), 1628-1639.

Cassman, K. G. and Munns, D. N. (1980). Nitrogen mineralization as affected by soil moisture, temperature and depth. *J. Soil Soc. Am.*, 44(6), 1233-1237.

Clarke, R. T., Leese, M. N. and Newson, A. J. (1973). Analysis of data from Plynlimon raingauge networks: April 1971-March 1973. *Inst. Hydrol. Rep. no.* 2[illegible].

Crisp, D. T. (1966). Input and output of minerals from an area of pennine moorland. The importance of precipitation, drainage, peat erosion and animals. *J. Appl. Ecol.*, 3, 327-348.

Cryer, R. (1976). The significance and variation of atmospheric nutrient inputs in a small catchment system. *J. Hydrol.*, 29(1/2), 121-137.

Cryer, R. (1980). The chemical quality of some pipeflow waters in upland mid-Wales and its implications. *Cambria*, 6(2), 28-46.

Dowdell, R. J. and Webster, C. P. (1976). Denitrification and leaching of nitrogen fertilizers: in Agriculture and Water Quality. *MAFF Technical Bulletin* no. 32, 163-173.

Edwards, A. M. C. (1973). The variation of dissolved constituents with discharge in some Norfolk rivers. *J. Hydrol.*, 18, 219-242.

Edwards, I. J., Jackson, W. D. and Fleming, P. M. (1974). Tipping bucket gauges for measuring runoff from experimental plots. *Agric. Meteorol.*, 13, 189-201.

Eriksson, E. (1952). Composition of atmospheric precipitation, 1, nitrogen compounds; 2, sulphur, chloride, iodine compounds, bibliography. *Tellus*, 4(3/4), 215-232 and 280-303.

Floate, M. J. S. (1970). Decomposition of organic materials from hill soils and pastures. III. *Soil Biol. Biochem.*, 2, 173-185.

Forestry Commission (1977). The wood production outlook in Britain.

Frissel, M. J. (Editor) (1977). Cycling of mineral nutrients in agricultural ecosystems. *Agro-Ecosystems*, 4, 1-354.

Gash, J. H. C., Wright, I. R. and Lloyd, C. R. (1980). Comparative estimates of interception loss from three coniferous forests in Great Britain. *J. Hydrol.*, 48, 89-105.

Heber, U. (1967). Freezing injury and uncoupling of phosphorylation from electron transport in chloroplasts. *Plant Physiol.*, 42, 1343-1350.

Heidel, S. G. (1956). The progressive lag of sediment concentration with flood waves. *Trans. Am. Geophys. Union*, 37, 56-66.

Henderson, G. S., Harris, W. F., Todd, D. E. Jr. and Grizzard, T. (1977). Quantity and chemistry of throughfall as influenced by forest-type and season. *J. Ecol.*, 65, 365-374.

Herman, F. A. and Gorham, E. (1957). Total mineral material, acidity, sulphur and nitrogen in rain and snow at Kentville, Nova Scotia. *Tellus*, 9, 180-183.

Hill, A. R. (1978). Factors affecting the export of nitrate-nitrogen from drainage basins in Southern Ontario. *Water Research*, 12, 1045-1057.

Holdsworth, P. M. and Roberts, G. (1982). A flow-proportional sampler for plot and lysimeter studies. *J. Hydrol.*, 57, 389-393.

IH Report No. 33 (1976). Water balance of the headwater catchments of the Wye and Severn. Inst. Hydrol., Wallingford, Rep. No. 33.

Institute of Hydrology (1980). The effects of land improvement on the discharge from upland pastures. An interim report on a joint IH/ADAS study at Plynlimon, mid-Wales.

Job, D. A. and Taylor, J. A. (1978). The production, utilization and management of upland grazings on Plynlimon, Wales. *J. Biogeography*, 5, 173-191.

Kanwar, R. S., Johnson, H. P. and Kirkham, D. (1982). Transport of nitrate and gaseous denitrification in soil columns during leaching. *J. Hydrol.*, 55(1/4), 171-185.

Martin, R. P. and White, R. E. (1982). Automatic sampling of stream water during storm events in small remote catchments. *Earth surface processes*, 7(1), 53-61.

Miller, H. G., Cooper, J. M. and Miller, J. D. (1976). Effect of nitrogen supply on nutrients in litterfall and crown leaching in a stand of Corsican pine. *J. Ap. Ecol.*, 13, 233-248.

Miller, H. G. (1979). The nutrient budgets of even-aged forests: in E. D. Ford, D. C. Malcolm and J. Atterson (eds). Procs. meeting of Div. IUFRO, Edinburgh, 1978

Munro, J. M., Davies, D. A. and Thomas, T. A. (1973). Potential pasture production in the uplands of Wales - no. 3. Soil nutrient resources and limitations. *J. British Grassland Society*, no. 28, 247-255.

Newbould, P. and Floate, M. J. S. (1977). Agro-ecosystems in the UK, Ch. 6.2: in Cycling of mineral nutrients in agricultural ecosystems. Ed. M. J. Frissel. *Agro-ecosystems*, 4, 1—354.

Newson, M. D. (1976). The physiography, deposits and vegetation of the Plynlimon catchments. *Inst. Hydrol. Rep. no. 30.*

Newson, M. D. (1980). The geomorphological effectiveness of floods - a contribution stimulated by two recent events in mid-Wales. *Earth Surface Processes*, 5, 1-16.

Oborne, A. C., Brooker, M. P. and Edwards, R. W. (1980). The chemistry of the River Wye. *J. Hydrol.*, 45(3/4), 233-253.

O'Loughlin, E. M. (1981). A rate of rise controller for automatic water samplers. *J. Hydrol.*, 50(1/3), 383-389.

Painter, R. B., Blyth, K., Mosedale, J. C. and Kelly, M. (1974). The effect of afforestation on erosion processes and sediment yield: in Effects of man on the interface of the hydrological cycle with the physical environment. Proceedings of the Paris Symposium, September 1974. *IASH-AISH Publ. no.* 113.

Reid, J. M., MacLeod, D. A. and Cresser, M. S. (1981). Factors affecting the chemistry of precipitation and river water in an upland catchment. *J. Hydrol.*, 50, 129-145.

Rolfe, G. L., Akhtar, M. A. and Arnold, L. E. (1978). Nutrient fluxes in precipitation, throughfall and stemflow in an Oak-Hickory forest. *Water Res. Bull.*, 14(5), 1220-1226.

Roberts, M. E. and James, D. B. (1972). Some effects of forest cover on nutrient cycling and river temperature. In: *Research papers in forest meteorology.* (Ed: J. A. Taylor) Cambrian News, Aberystwyth, 100.

Stanford, G. and Epstein, E. (1974). Nitrogen mineralization - water relations in soils. *Soil. Sci. Soc. Am. Proc.*, 38, 103-107.

Stanford, G. and Smith, S. J. (1976). Estimating potentially mineralizable soil nitrogen from a chemical index of soil nitrogen availability. *Soil Sci.*, 122(2), 71-76.

Stenlid, G. (1958). Salt losses and redistribution of salts in higher plants. *Handb. Pfl Physiol.*, 4, 615-637.

Terry, R. E. (1980). Nitrogen mineralization in Florida Histosols. *Soil Sci. Soc. Am. J.*, 44(4), 747-750.

Timmons, D. R., Holt, R. F. and Latterall, J. J. (1970). Leaching of crop residues as a source of nutrients in surface runoff water. *Water Resour. Res.*, 6(5), 1367-1375.

Walling, D. E. and Foster, I. D. L. (1975). Variations in the natural chemical concentration of river water during flood flows, and the lag effect: some further comments. *J. Hydrol.*, 26(3/4). 237-244.

Walling, D. E. and Webb, B. W. (1981). Chap. 5 in *Water quality in British rivers,* (Ed: J. Hewin) George Allen & Unwin.

Whitehead, H. C. and Feth, J. H. (1964). Chemical character of rain, dry fallout and bulk precipitation at Menlo Park, California, 1957-1959. *J. Geophys. Res.*, 69(16), 3319-3333.

ACKNOWLEDGEMENTS

The encouragement and funding given by the Ministry of Agriculture, Fisheries and Food to this study is much appreciated. In particular, the authors wish to thank the staff of MAFF Trawscoed for analysing the considerable number of water samples collected during the course of this study.