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Nutrient budgets in a dry heathland watershed in northeastern Spain

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Abstract. Dissolved nutrient inputs in bulk precipitation and outputs in streamwater were measured during 3 years of contrasting hydrological conditions in a 6.3-ha, grazed heathland watershed on schists in the Montseny mountains (NE Spain), drained by an intermittent stream. On average, 39% of the precipitation became streamflow. Bulk precipitation delivered positive net alkalinity (mean 0.22 keq/ha/yr), sulphate input was moderate (9.0 kg SO_4-S/ha/yr), and the mean input of inorganic N was not exceptionally high (6.6 kg/ha/yr). Ion concentrations were relatively low in streamwater; SO_4^{2-} was the dominant anion. Most concentrations in streamwater varied seasonally, with maxima in late summer or early autumn and minima in spring. This pattern probably resulted from increased availability of ions for leaching due to decomposition of organic matter and chemical weathering during the warm period. Nitrate concentrations were relatively high in winter and dropped sharply in early spring, probably because of biological uptake. Annual element outputs in streamwater varied between years and seemed to be controlled by both the amount of annual streamflow and its seasonal distribution. Annual inputs exceeded outputs for dissolved inorganic N. The watershed accumulated H^+ and Ca^{2+}, had net losses of Na^+ and Mg^{2+}, and was close to steady state for K^+, SO_4^{2-}, Cl^- and alkalinity. The chloride budgets gave no evidence of substantial dry deposition in this system. The cationic denudation rate was negative (−0.14 keq/ha/yr) because Ca^{2+} retention was higher than net exports of Na^+ and Mg^{2+} from silicate weathering. Low nutrient export and little production of alkalinity suggest that this watershed has a low buffering capacity.

Introduction

Most heathland soils are nutrient-poor and strongly acidic (Specht 1979). Some heathland plants, such as *Calluna vulgaris*, are thought to exacerbate soil acidification and podsolization (Miller 1981), and frequent fires increase nutrient losses from heathlands (Hobbs & Gimingham 1987). Mineral weathering and atmospheric nutrient inputs are important nutri-

ent sources. However, high rates of nitrogen deposition in industrialized countries can be deleterious for the integrity of heathland ecosystems because heathland species tend to be displaced by grasses when nitrogen availability is high (van Breemen & van Dijk 1988).

Upland heathlands often occur in headwater areas that are important for water supplies. In northwestern Europe, many heathlands receive strongly acidic atmospheric deposition, increasing the proton load of already acidic soils (e.g. Ulrich & Pankrath 1982). Therefore, neutralization of acidic inputs within the heathland ecosystem is important for downstream water quality. In spite of the crucial role that nutrients and acidity play in the ecology of heathlands, relatively few watershed nutrient budgets exist for heathlands as compared to forest ecosystems. Nutrient studies at the watershed level in heathlands have dealt with atmospheric inputs (Cryer 1976), peat erosion and the effects of animals (Crisp 1966), weathering rates as controlling factors of streamwater chemistry (Edwards et al. 1984; Reid et al. 1981), and the effects of rotational burning (Dauge 1986; Hughes 1984). More information on nutrient distribution and cycling in heathlands is available at the plot level (e.g. Chapman 1967; Fogeard et al. 1979; Matzner & Ulrich 1980).

In the Montseny mountains of NE Spain, heathlands occupy a landscape similar to that of northwestern Europe. This area has been identified as potentially sensitive to acidification (Bonilla 1985). This paper presents nutrient concentrations and fluxes in bulk precipitation and streamwater over a three-year period in a small, grazed dry heathland watershed at Montseny.

Study area

The study was conducted at the Estació Biològica de La Castanya in the Montseny Natural Park and Biosphere Preserve, 40 km NNE of Barcelona. The instrumented watershed (TM5; Fig. 1) is located near the summit of La Calma, a dissected rolling plateau whose upper reaches have been deforested to provide grazing lands and some arable fields.

TM5 is 6.3-ha, NW-facing headwater catchment with an intermittent stream. Its altitude ranges from 1240 to 1335 m above sea level, and it has a mean slope of 13°. There are no weather stations at La Calma, but from data at other localities within Montseny, mean annual temperature at TM5 is estimated to be 8—9°C, and mean annual precipitation 850—900 mm. Snow accounts for about 10% of the annual precipitation, usually persisting on the ground for some days to several weeks after major snowfalls. The underlying bedrock is a metamorphic schist with quartz,

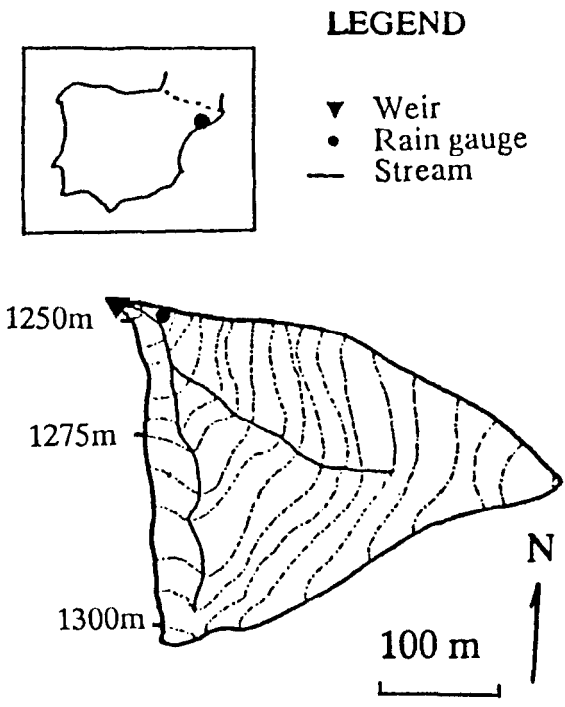

Fig. 1. Location map for the study watershed at La Calma (Montseny).

albite, muscovite and chlorite as major minerals. Soils are rather shallow (50—60 cm) dystric xerochrepts, with a sandy-loam texture; they are acidic (mean pH in KCl 4.4) and have a low base saturation. Vegetation is described in detail by Perrinet (1988). The upper 70% of the watershed was abandoned from agriculture in 1960—1963 and presently covered by a grassy heathland dominated by *Cytisus scoparius*, a shrub 1—2 m tall. The lower 30% is covered by a dense *Calluna vulgaris* heathland. A strip of bracken-dominated grassland follows the stream. The catchment is grazed by sheep and cattle. Fire has not occured in the *Cytisus* heathland of TM5 since the abandonment of the fields some 21—24 years prior to this study. The mature *Calluna* heathland has not been burned for several decades.

Methods

Precipitation volumes were measured near the watershed outlet with one recording and one non-recording rain gauge. Differences between the

gauges were usually less than 10%, and their total precipitation volumes during two years differed by only 0.8%. During an 11-month period precipitation was additionally measured in a network of 9 wedge gauges evenly distributed within the watershed. The mean precipitation measured during this period was 546 mm in the network and 552 mm in the non-recording gauge. It was concluded that point precipitation measured at the watershed outlet was representative of areal precipitation within the 6.3-ha watershed. Snowfall was measured with a bucket 60 cm tall and 33 cm in diameter, lined with a clean polyethylene bag.

Streamflow was continuously recorded at the watershed outlet in a gaging station equipped with a sharp-crested 60° V-notch weir and a Weather-Measure stage recorder. The relationship between stage and instantaneous discharge was determined by measuring discharge, using a bucket and stopwatch technique, for a wide range of flow rates.

Bulk precipitation was sampled in three polyethylene collectors adjacent to the rain guages at the watershed outlet. Each collector consisted of a 19-cm diameter funnel connected by PVC tubing to a 10-L container. All plastic containers used to sample precipitation and streamwater for chemical analyses were washed with diluted HCl and thoroughly rinsed with distilled water. Extensive conductivity checks and blank trials were conducted to ensure that no contamination by residual HCl occurred.

Sampling was done on a weekly or sometimes biweekly basis. At each sampling date, the bulk precipitation collectors were retrieved and replaced by clean ones. If no precipitation had occurred during the sampling period, dry fallout in the funnels was recovered by rubbing their inner sides with a plastic glove and rinsing them with distilled water. Grab samples of streamwater were taken above the weir. These were supplemented during storm events by samples taken by a Manning 4040 sampler that automatically switched on when a given stage was reached at the weir. This sampler took up to 24 streamwater samples at fixed time intervals, predetermined depending on the expected hydrological conditions. Sampling frequencies ranged from 15—30 minutes for fast summer storms to 2—6 hours for longer hydrographs under wet antecedent conditions.

After collection, samples were taken to the laboratory and immediately analyzed for pH and conductivity at 20 °C by electrochemical methods, and for positive alkalinity by conductimetric titration. Samples were stored at −25 °C awaiting further analyses. Metallic cations were analyzed in the presence of HCl and La. Sodium and K^+ were analyzed by flame emission, and Ca^{2+} and Mg^{2+} by atomic absorption spectrometry. Ammonium, NO_3^-, SO_4^{2-} and Cl^- were analyzed by ion chromatography on a Dionex 2010i system. Analytical accuracy was assessed with a synthetic rainwater solution. Accuracy was within 6% for each of the analyzed

ions (data for NH_4^+ not available). HCO_3^- was assumed to be equal to alkalinity for samples having positive alkalinity.

The particulate component of bulk precipitation was not systematically measured during the present study. Turbid bulk precipitation samples were filtered through 0.45-μm Millipore filters after conductivity, pH and alkalinity measurements.

Element inputs in bulk precipitation were obtained by multiplying the volume-weighted mean (VWM) ion concentrations by the appropriate amount of precipitation. Inputs in dry fallout during dry periods were computed from ion concentrations and the volumes of rinsing water. Dissolved nutrient outputs in streamwater were computed as the sum of the products of ion concentrations and time-weighted streamflow calculated for all sampling intervals in a given year. Alkalinity for 7% of the annual precipitation in 1984 was estimated from multiple regression analysis using available measured concentrations of other ions.

Results

Water fluxes

The three years of study had contrasting precipitation patterns. 1983 was a moderately dry year (742 mm) in which spring rains were scarce and 55% of the annual precipitation occurred in autumn. 1984 was moderately wet (1008 mm) with spring and autumn rains about equally abundant, and with relatively high summer rainfall. 1985 was very dry (605 mm), and spring was the rainiest season, with 44% of the yearly precipitation. The mean annual precipitation during this 3-year period was 785 mm, 8—13% lower than the estimated long term mean at this site (850—900 mm). Snowfall accounted on average for 12% of the annual precipitation. As is usually the case in Mediterranean climates, the monthly amounts of precipitation were highly variable, with long dry spells and a few months of copious rainfall. The four wettest months in this study (November 1983, May and November 1984, and May 1985) accounted for 37% of the total precipitation received during the three years. In spite of this high temporal aggregation, precipitation intensities were only moderate. The mean of the maximum hourly intensities during 1983—1984 for rainfall events delivering $\geqslant$ 10 mm was 11.4 mm/h (S.D. 7.9).

Most precipitation events did not generate appreciable streamflow because water was retained in the dry soils, or in some winter events, water was accumulated in the snowpack. The intermittent character of the

stream draining TM5 is evident in Figure 2. Some stream discharge data in November—December 1983 were missing, and the total streamflow for this period was estimated from other storm events. During the 3-year study period only about 8 different storm hydrographs, each with a duration of 2—6 weeks, were observed. After major storms, recessions were rapid and the stream was virtually dry a few weeks after even the largest events (Fig. 2).

Annual streamflow increased with annual precipitation. Mean annual streamflow was 309 mm, or 39% of the mean annual precipitation. The mean annual evapotranspiration averaged over the watershed was 476 mm, and varied surprisingly little between years (1983: 458 mm, 1984: 524 mm, 1985: 447 mm). These figures are similar to comparable evapotranspiration estimates in heathland watersheds from northern and southern England (Hughes 1984; Wallace et al. 1982).

Bulk precipitation chemistry

On a stoichiometric basis, there was an excess of cations over anions in bulk precipitation (Table 1). The cation surplus ranged between 16—12% for single years (1983 and 1984; 1985 no data), but was only 7% for the calculated bulk precipitation annual mean. Bulk precipitation chemistry was dominated by Ca^{2+} and SO_4^{2-} (Table 1), which together accounted for 45% of the analyzed ion equivalents. Sodium and Cl^- were strongly

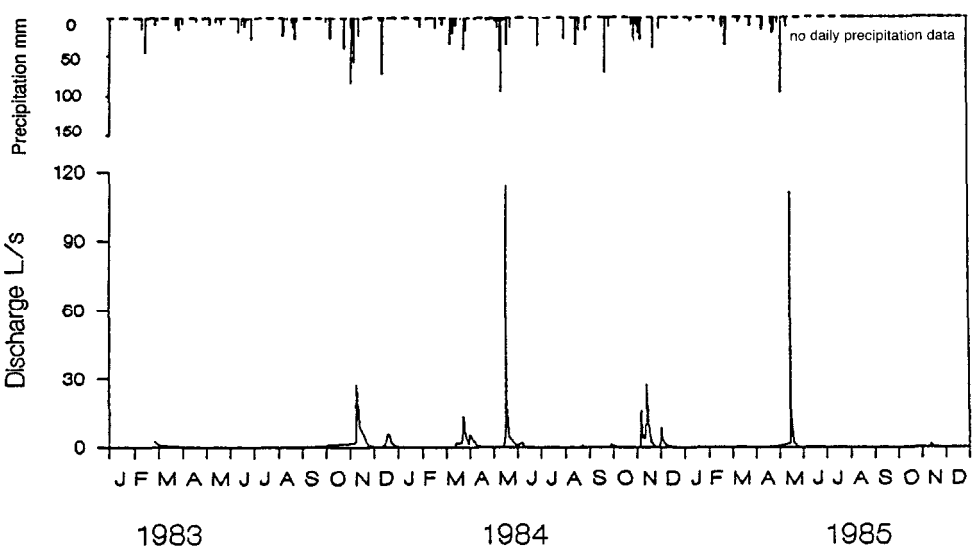

Fig. 2. Temporal distribution of instantaneous discharge and daily precipitation at TM5.

Table 1. Volume weighted mean annual chemical concentrations in bulk precipitation in a heathland watershed (TM5) at Montseny. Concentrations in μeq/L.

Year	(mm)	Cond.[a] (μS/cm)	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	NO_3^-	SO_4^{2-}	Cl^-	Alk[b]	Alk[c]
1983	742	23.1	18.2	29.2	3.4	82.1	13.0	32.6	25.4	71.1	40.6	16.3	−1.9
1984	1008	24.3	13.7	36.9	4.6	102.4	18.4	27.3	23.9	67.3	40.4	49.8[d]	36.1
1985	605	21.0	22.2	16.9	3.8	76.9	12.5	—	27.0	66.9	25.8	—	—
Mean[e]	785	23.1	17.3	29.3	4.0	89.5	15.2	29.6	25.2	68.4	36.7	35.6	20.0
S.D.	205	1.3	3.5	8.0	0.5	11.4	2.8	2.6	1.3	1.8	6.4	16.6	18.8

[a] Electrical conductivity
[b] Positive alkalinity
[c] Net alkalinity
[d] Partially estimated (see text)
[e] precipitation-weighted annual mean and standard deviation

correlated and their ratio in bulk precipitation was close to that of seawater, implying that the major source was sea-salt aerosols. The volume weighted mean annual (VWM) concentrations of Na^+ and Cl^- in bulk precipitation (Table 1) indicated that the maritime influence was only moderate. Using Na^+ as a reference ion, and assuming no fractionation occurred during their emission, transport and deposition, sea-salt aerosols contributed the following percentages to the VWM ion concentrations in bulk precipitation at TM5: Cl^- 90, Mg^{2+} 44, K^+ 14, Ca^{2+} 1, and SO_4^{2-} 5. Most SO_4^{2-} must be of anthropogenic origin, though a minor part could be biogenic or volcanic (Vong 1990). Most of the NH_4^+ and NO_3^- is also probably anthropogenic.

A principal components analysis of bulk precipitation samples for 1982—1984 at TM5 (Belillas 1989) produced the following grouping of chemical variables:

- Na^+ and Cl^-, representing the marine contribution;
- pH, alkalinity and Ca^{2+}, representing calcareous dust; and
- SO_4^{2-}, NH_4^+ and NO_3^-, representing urban and industrial air pollution.

Magnesium and K^+ lay in intermediate positions among these groups. Such a grouping of chemical variables is useful for summarizing the major influences on bulk precipitation chemistry at our site, but it should not be taken as a sharp classification. For example, positive alkalinity can only account for less than half of the Ca^{2+} (Table 1), so a large part of the positive charge due to Ca^{2+} must be balanced by negative charge due to SO_4^{2-}.

The pH of weekly bulk precipitation samples ranged from 3.9 to 7.5 in this study. Strongly acidic precipitation (pH $<$ 4.5) occurred in 23 out of 99 weekly samples. These strongly acidic events delivered 16% of the precipitation. The 3-year VWM H^+ concentration, computed from pH values without taking into account neutralization by alkaline events, was 17.3 μeq/L (pH 4.76), suggesting that bulk precipitation was on average moderately acidic (Table 1). However, it is invalid to assess annual precipitation acidity as the annual mean of H^+ concentrations when strongly acidic, less acidic and basic precipitation events occur at a given site (Liljestrand 1985, Young et al. 1988). The VWM positive alkalinity, determined by assigning 0 alkalinity to samples, with pH $<$5, for which alkalinity was not measured, was about equal to (1983) or much greater than (1984) the VWM H^+ concentration computed from pH (Table 1; alkalinity data for 1985 not available). The annual mean net alkalinity in bulk precipitation computed from 1983 and 1984 data was 20 μeq/L, revealing that bulk precipitation at TM5 had positive alkalinity.

Streamwater chemistry

Budgets for streamwater chemistry were generally well balanced with respect to cations and anions. Charge discrepancies were < 10% for single years, and < 1% for the three-year mean. Streamwater at TM5 was dominated by SO_4^{2-}, Ca^{2+} and Na^+ (Table 2). It had a mean pH of 6.0 and a moderate but positive alkalinity (VWM 61 μeq/L). Though such chemistry is common in temperate streams, it is rather unusual at Montseny. TM5 and other adjacent streams at La Calma (Belillas 1989), stand apart from most other streams draining schist watersheds in the Montseny mountains (Avila 1984) because of their low ion concentrations, very low pH and alkalinity, and SO_4^{2-} anion dominance.

The concentrations of most ions were negatively correlated with stream discharge. However, the absolute magnitude of the Kendall's rank correlation coefficients was relatively low (< 0.4). In part, these relatively weak correlations resulted from seasonal variations in concentration-discharge relationships. At high flows, ion concentrations were always higher in November than in May. This may be associated with the availability of ions for leaching at the time of major storms. During late spring and summer, relatively high temperatures probably increase the rates of biological decomposition of organic matter and mineral weathering. Ions released by these processes are likely to remain within the watershed since there is virtually no streamflow during the warm period. Some of these ions can then be leached during the first major autumn storms. Conversely, after a relatively cool winter, fewer ions would be available for leaching into streams (Feller 1977). In our study, these interactions between temperature, streamflow regime, biological activity, and weathering rates could account for the differences in ion concentrations in streamwater between November and May storms.

Concentrations of most ions exhibited annual cycles with minima in spring and maxima during summer storms that generated little streamflow. Concentrations were also high during the first major autumn storm (Fig. 3). Bicarbonate exhibited the opposite trend. Sulphate concentrations were highly variable, without an apparent seasonal trend. Nitrate followed the same pattern of most ions but with variations that were probably due to biotic regulation. Nitrate concentrations were relatively high during snowmelt periods in late winter, indicating either that NO_3^- was being released from the snowpack (NO_3^- in streamwater at these times was never above 40 μeq/L, Fig. 3) or that nitrification rates were high during freezing periods (Likens et al. 1977). In each of the three years, NO_3^- decreased in streamwater during spring (Fig. 3) probably because of increased plant and microbial uptake.

Table 2. Volume weighted mean annual chemical concentrations in streamwater in a heathland watershed (TM5) at Montseny. Concentrations in μeq/L.

Year	(mm)	Cond.[a] (μS/cm)	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NO_3^-	SO_4^{2-}	Cl^-	Alk[b]
1983	284	40.5	0.8	121	11.7	155	67	28.4	188	109	65
1984	484	35.9	0.7	120	7.0	150	72	12.9	183	76	62
1985	158	32.0	2.2	104	4.7	121	63	8.1	159	52	51
Mean[c]	309	36.7	1.0	118	8.1	146	69	16.8	180	82	61
S.D.	164	2.9	0.6	6	2.6	12	3	7.9	10	20	5

[a] Electrical conductivity
[b] Positive alkalinity
[c] Streamflow-weighted annual mean and standard deviation

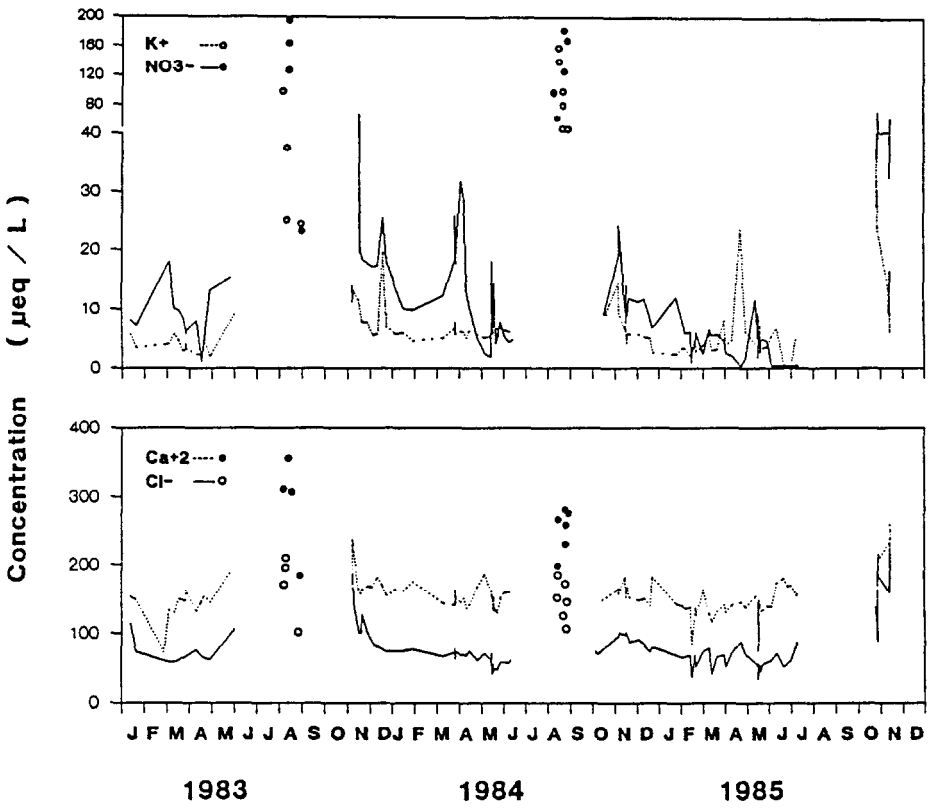

Fig. 3. Seasonal variation of selected ion concentrations in streamwater at TM5.

Nutrient fluxes

Precipitation inputs

Dry fallout supplied only limited amounts of soluble elements to the TM5 watershed. Expressed as percent of bulk precipitation, dry fallout contributed less than 4% to the annual mean inputs of ions such as NH_4^+ and SO_4^{2-} which, as dry fallout, are derived from very small atmospheric particles or from gases (e.g. Lindberg et al. 1986). Dry fallout contributed slightly more to the annual deposition of elements, which, as dry fallout, are contained in larger particles: K^+ 13%, Mg^{2+} 11% and Ca^{2+} 10%.

On a mass basis, bulk precipitation inputs were dominated by Ca^{2+}, Cl^-, and SO_4-S (Table 3). The calcium deposition rate was very high (annual mean 15 kg/ha). Sulphur input in bulk precipitation was moderate (9 kg SO_4-S/ha/yr). Inorganic N inputs were rather low (6.6 kg N/ha/yr)

with NH_4-N accounting for 56% of this. The mean annual input of free acidity was 0.14 keq/ha, much lower than the range of 0.4–1.5 keq/ha/yr (bulk precipitation) prevailing in many areas of central and northern Europe (Adriano & Havas 1989; Brechtel 1989). Furthermore, the mean input of positive alkalinity in bulk precipitation at TM5 was 0.36 keq/ha/yr, more than double the free acidity input. Overall, the heathland ecosystem at TM5 does not appear to be under stress from atmospheric deposition of acid, S, or N.

Element inputs in bulk precipitation showed considerable variation between years. Coefficients of variation ranged from very low (H^+ 4%, NH_4-N 8%, the latter based on only two years of data) to moderate (NO_3-N 18%, SO_4-S 23%) to high (K^+ 31%, Ca^{2+} 36%, Mg^{2+} 39%, Cl^- 40%, Na^+ 52%). At this level of variability, 10-25 years of data would be required to reduce the standard error of the annual inputs for the last group of ions to within 10% of the mean. As the coefficient of variation of annual precipitation in this study was 26%, yearly differences in precipitation amounts account for only part of the variability in annual deposition. In fact, bulk precipitation inputs were much higher in 1984 than in either 1983 or 1985 for every ion except H^+, (Table 3). This resulted both from higher precipitation and from higher VWM concentrations of Na^+, K^+, Ca^{2+}, Mg^{2+}, and alkalinity during 1984 (Table 1). Relatively low H^+ inputs in 1984 might be explained by neutralization of H^+ in the atmosphere by relatively large amounts of $CaCO_3$ particles in the atmosphere that year. The very high concentrations and inputs of Ca^{2+} and alkalinity in 1984 stem from the occurrence of major "red rains" that year. Red rains in the Mediterranean region are produced by long-range transport of Saharan dust (Löye-Pilot et al. 1986). They are laden with calcite-bearing silt particles, are much more alkaline and Ca-rich than other rains, and strongly influence the mean chemistry and annual element inputs at Montseny (Avila & Rodà 1991; Belillas 1989). At TM5, the 13 red rain events, recorded during this study, had concentrations 2–7 times greater than other precipitation events. A single red rain event of 84 mm on November 1984 delivered 5.3 kg Ca^{2+}/ha, or 25% of the total Ca^{2+} input that year.

Streamwater outputs

On a mass basis, dissolved streamwater outputs were dominated by Ca^{2+}, Cl^-, SO_4–S and Na^+ (Table 3). For most ions, annual outputs in streamwater decreased in the order 1984 > 1983 > 1985, the same order as annual streamflow and for the annual nutrient input in bulk precipitation, which is strongly dependent on annual precipitation. Coefficients of variation in annual output were 57% to 65% for all analyzed ions except H^+ (data for NH_4^+ not available). Thus, yearly variation in output was

considerably greater than for input. This resulted largely from annual streamflow being more variable (CV 53%), in relative terms, than annual precipitation. Additionally, and contrary to expectation, the year with the lowest streamflow (1985) also had the lowest VWM concentrations for all ions except H^+ (Table 2), helping to increase the variability in annual element outputs. The low ion concentrations and outputs in streamwater during 1985 can be traced back to the dominance of spring streamflow, as discussed above.

Monthly output of total analyzed elements except H^+ was more strongly correlated with monthly streamflow ($r = 0.98$, $P < 0.001$, $n = 16$) than with monthly inputs in bulk precipitation ($r = 0.63$, $P < 0.05$) (Fig. 4). Most (70%) of the total output in streamwater during the 3 years took place during the four months with the highest precipitation and streamflow (Fig. 4).

Watershed nutrient budgets

In spite of the large hydrological differences between years in this study, there were very few yearly changes in the sign of element budgets (Table 3). In each of the three years, inorganic N inputs by bulk precipitation were greater than streamwater outputs. The watershed apparently also retained H^+, Ca^{2+} and Cl^-, and released Na^+ and Mg^{2+}. Net inputs of K^+ were positive in 1984 and 1985, but negative, albeit close to zero, in 1983. Net inputs of SO_4-S were quite variable: small but positive in 1983, relatively large and negative in 1984, and relatively large and positive in 1985, with a 3-year mean very close to zero (Table 3). Alkalinity showed a zero net input in 1983 and a positive input in 1984 (no data for 1985). On average, net inputs were positive for H^+, K^+, Ca^{2+}, inorganic N, Cl^- and alkalinity, negative for Na^+ and Mg^{2+}, and close to zero for SO_4-S. During the 3-year period of study H^+, Ca^{2+}, NH_4-N and NO_3-N annual net inputs were consistently positive and exhibited relatively low annual variations (mean net inputs for these parameters had the lowest coefficients of variation). This would suggest that net inputs of these elements were greater than zero, but having only 3 years of data precludes a definitive statistical analysis.

At TM5 Cl^- had an average net input of 1.9 kg/ha/yr. This was strongly influenced by the net input of 3.4 kg/ha measured in 1985. This year was the driest in 40 years of record at the weather station at the summit of Montseny (1700 m a.s.l.). As autumn streamflow virtually failed in 1985, a substantial part of the Cl^- input during this year was probably leached in subsequent year(s), thus leading to overestimation of the net Cl^- input. A better estimate of the mean Cl^- budget is probably provided by the average of 1983 and 1984. For these two years, the mean annual

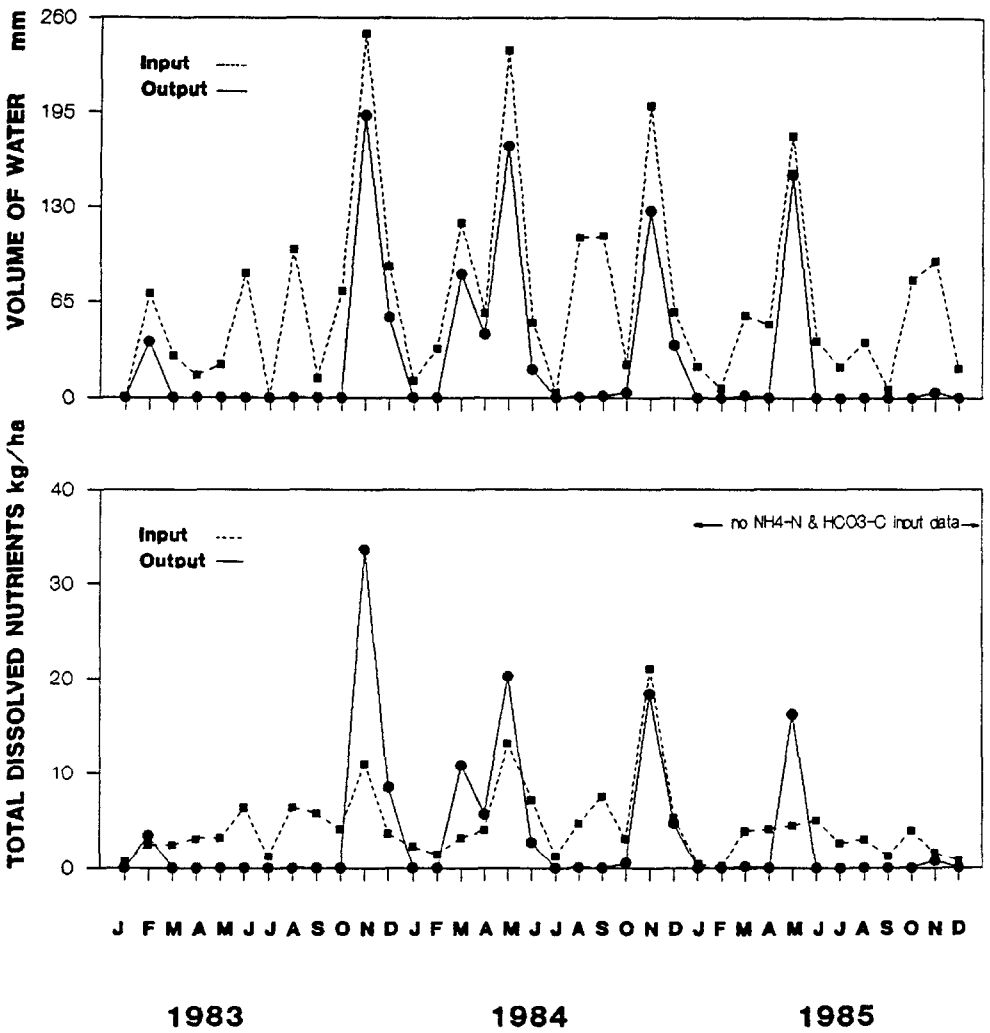

Fig. 4. Monthly input and output fluxes of water (*top*) and total dissolved nutrients (*bottom*) in the study watershed (TM5).

precipitation of 875 mm was very close to the estimated long-term mean, and the seasonal distribution of precipitation and streamflow (Fig. 4a) favoured leaching of most the Cl^- input. That the mean net input of Cl^- for 1983 and 1984 was close to zero 1.1 kg/ha/yr might suggest that unmeasured dry deposition of Cl^- was of little importance in this watershed. This finding agrees with throughfall (Ferrés et al. 1984) and watershed Cl^- fluxes (Alvila & Rodà 1988) in a nearby holm oak forest

Table 3. Annual bulk precipitation input and streamflow output fluxes (kg/ha/yr) of dissolved elements in a small heathland watershed (TM5, Montseny)

Budget	Water flux (mm)	H^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4-N	NO_3-N	SO_4-S	Cl^-	HCO_3-C
Inputs											
1983	742	0.14	5.5	1.2	14.0	1.4	3.5	2.8	8.9	11.4	2.2
1984	1008	0.14	8.7	1.9	21.5	2.3	3.9	3.5	11.1	14.8	6.3
1985	605	0.13	2.8	1.1	10.8	1.1	—	2.5	6.9	6.3	—
Mean	*785*	*0.14*	*5.7*	*1.4*	*15.4*	*1.6*	*3.7*	*2.9*	*9.0*	*10.8*	*4.3*
(S.D.)		(0.01)	(3.0)	(0.4)	(5.5)	(0.6)	(0.3)	(0.5)	(2.1)	(4.3)	(2.9)
Outputs											
1983	284	0.00	7.9	1.3	8.8	2.3	0[b]	1.1	8.6	11.0	2.2
1984	484	0.00	13.4	1.3	14.5	4.2	0	0.9	14.2	13.0	3.5
1985	158	0.00	3.8	0.3	3.8	1.2	0	0.2	4.0	2.9	1.0
Mean	*309*	*0.00*	*8.4*	*1.0*	*9.0*	*2.6*	*0*	*0.7*	*8.9*	*9.0*	*2.2*
(S.D.)		(0.00)	(4.8)	(0.6)	(5.4)	(1.5)	(0)	(0.5)	(5.1)	(5.3)	(1.3)
Net inputs[a]											
1983		0.14	−2.4	−0.1	5.2	−0.9	3.5	1.7	0.3	0.4	0.0
1984		0.14	−4.7	0.6	7.0	−1.9	3.9	2.6	−3.1	1.8	2.8
1985		0.13	−1.0	0.8	7.0	−0.1	—	2.3	2.9	3.4	—
Mean		*0.14*	*−2.7*	*0.4*	*6.4*	*−1.0*	*3.7*	*2.2*	*0.0*	*1.9*	*1.4*
(S.D.)		(0.01)	(1.9)	(0.5)	(1.0)	(0.9)	(0.3)	(0.5)	(3.0)	(1.5)	(2.0)

[a] Net inputs = inputs-outputs

[b] Not measured but probably less than 0.1 kg/ha/year.

(only 1.35 km from TM5), where the input of Cl^- by aerosol impaction of marine salts was estimated to be 0.7 kg/ha/yr.

As in most vegetated, undisturbed watersheds NH_4-N and NO_3-N were apparently retained within TM5, giving a net input of 6.6 kg/ha/yr of inorganic N to this heathland ecosystem. However, the complete watershed N budget is unknown, since other N fluxes (dissolved organic N, particulate and gaseous fluxes) were not measured. Denitrification and symbiotic fixation fluxes could account for substantial N outputs and inputs, respectively, in this grazed watershed with *Cytisus scoparius* vegetation. As in many systems under extensive grazing, volatilization of NH_3 is likely to occur from animal excreta (Floate 1981). In addition *Cytisus scoparius* has been found to fix about 35 kg N/ha/yr (Wheeler et al. 1987), and root nodules are present in *Cytisus scoparius* at TM5 (Bonilla 1990).

Assuming inputs by dry deposition are negligible, net losses of Na^+ and Mg^{2+} at TM5 probably resulted from chemical weathering of Na- and Mg-bearing silicate minerals (mainly albite and chlorite, respectively). The low net losses of both elements (Table 3) strongly suggest low weathering rates at this culminal location. In contrast, in a nearby forested watershed at lower altitude and where the lithology has been classified as the same metamorphic schist underlying TM5, net losses of Na^+ and Mg^{2+} were about 6 times greater than at TM5 (Avila & Rodà 1988).

Calcium from bulk precipitation was accumulated within the TM5 watershed (Table 3). Positive net inputs of Ca^{2+} were observed even in the moderately wet year (1984). Yearly net inputs of Ca^{2+} were much less variable (CV 16%) than either inputs or outputs. The Ca^{2+} accumulation rate is probably higher than that indicated by the budgets of soluble Ca^{2+}, since there is a considerable input of particulate Ca^{2+} in bulk precipitation, particularly in red rains. Most studied watersheds have net losses of Ca^{2+} in streamwater, probably as a result of silicate weathering, depletion of soil exchangeable Ca^{2+}, or unmeasured aerosol impaction. A compilation of element budgets in 31 temperate and boreal forested watersheds on silicate bedrocks yielded a mean net output of 6.5 kg Ca^{2+}/ha/yr (Avila & Rodà 1988). Though uncommon, examples of Ca-accumulating watersheds exist in the literature (Hornung et al. 1990). At TM5, the rate of Ca^{2+} accretion in plant biomass is probably low to moderate since the populations of both *Cytisus* and *Calluna* are already mature, and the grasses should be more or less in steady state. Therefore, atmospheric Ca^{2+} is probably being retained in the soil, most likely on exchange sites.

The cationic denudation rate (CDR) of a watershed is here defined as the sum, on an equivalent basis, of the net outputs of metallic cations. CDR is useful as an indicator of the intensity of weathering (or depletion of exchange cations), and provides one of the best watershed-level

estimates of the acid neutralization capacity of terrestrial ecosystems (Thompson 1982). From Table 3, the average CDR at TM5 is −0.14 keq/ha/yr. The CDR is negative since retention (primarily of Ca^{2+} and K^{+}) exceeds release (primarily of Na^{+} and Mg^{2+}). In contrast, the CDR in the nearby holm oak forested watershed mentioned above is 1.3 keq/ha/yr (Avila & Rodà 1988). This suggests that the TM5 ecosystem had a very low ability to supply cations to percolating water. This was also reflected in the alkalinity budget. Bulk precipitation alkalinity inputs of −0.14 keq/ha/yr from free acidity, and 0.36 keq/ha/yr from events having positive alkalinity, gave a positive net alkalinity input of 0.22 keq/ha/yr. Alkalinity output in streamwater averaged 0.24 keq/ha/yr during 1983−1984 when the alkalinity inputs were measured (Table 3). Thus, inputs and outputs of alkalinity in solution were roughly balanced, and the TM5 ecosystem showed little capacity for generating alkalinity. There is probably an additional unmeasured input of atmospheric alkalinity as carbonate particles that may dissolve in the soil. The calcite inputs to this watershed by "red rains" can be high. During 1982, 1983 and 1984 a total of 10 red rains were identified and the deposition of particulate matter measured for four of them ranged between 2 and 68 kg/ha. Consequently, the studied watershed probably acts as an alkalinity sink.

Element budgets at TM5 are compared with those from several British heathland and other forested watersheds in Table 4. TM5 differs from the other watersheds due to its relative abundance of nutrient net gains, particularly Ca^{2+}. Most of the British heathlands had large net outputs of Na^{+} and Cl^{-}, a reflection of their greater exposure to maritime influences. In contrast to TM5, all the British heathlands studied exhibited net losses of Ca^{2+}, even those on silicate bedrock. Two Scottish heathlands (Glendye and Peatfold-Glenbuchat), were similar to TM5 in that they were on metamorphic or igneous felsic rocks and had very high CDRs (1.7 and 1.6 keq/ha/yr values calculated after correcting for sea-salt aerosol impaction with the criterion of a balanced Cl^{-} budget). These differences between TM5 and the other watersheds presumably result from abiotic watershed-specific factors, such as proximity to ocean, bedrock type and weathering rate, base saturation level in soils, drainage patterns and the occurrence of highly concentrated Ca-rich red rains at Montseny.

Overall, nutrient budgets at TM5 for the 3-year period showed a dominance of net gains over net losses. Although TM5 had low weathering rates and soil-acidifying vegetation, which makes it particularly sensitive to nutrient deficits and gives it a very low H^{+} buffering capacity, we have found this watershed to retain nutrients, including H^{+} ions, very efficiently. However, this watershed was not under stress from acidic deposition which can be attributed to the occurrence of basic red rains

Table 4. Annual nutrient budgets (kg/ha/yr) for some heathland and selected forested watersheds.

Location	Area	Altitude[a]	Vegetation	Geology	Management	R/P[b]	Na^+	K^+	Ca^{+2}	Mg^{+2}	N[c]	SO_4-S	Cl^-
Heathlands													
TM5 (this study)	6.3	1288	*Cytisus -Calluna*	Metamorphic schist	Grazing	0.39	−2.7	0.44	6.4	−1.0	5.9	0.03	1.9
Rough Sike[1] (England)	83	625	Bog	Sedimentary carbonate shale and sandstone	Grazing	0.81	−19.7	−5.9	−44.8	—	5.2	—	—
Maesnant[2] (Wales)	—	—	Bog	Sedimentary shale and sandstone	—	—	−16.5	−1.0	—	−4.3	—	—	—
Wet Sleddale[3] (England)	1214	—	Heather and peat bogs	Andesite and granite	Grazing	—	−20.5	−3.9	−26.9	−11.4	—	14.0	−23.4
Glendye[4] (Scotland)	4120	389	Heather (*Calluna*)	Granite and Gneis	Grazing, rotational burning	0.86	−29.3 (−8.9	−3.3 −2.9	−19.6 −17.0	−7.6 −5.0	— —	−7.6 0.0	−31.7 0.0)[d]
Peatfold[5]-Glenbuchat (Scotland)	200	—	Moorland	Norite Shale and Granite	Grazing, rotational burning	—	−10.9 (−2.2	−2.5 −1.2	−21.7 −20.2	−6.6 −5.9	— —	6.7 0.0	−9.8 0.0)[d]
Withybed[6] Bottom (England)	128	—	Heather (*Calluna*)	Sedimentary	Grazing, burning	0.42	—	−1.3	−6.3	−3.3	—	—	—
Forests[7]													
x	—	—	—	—	Undisturbed	0.37	−7.4	−1.4	8.7	−3.3	4.5	−1.1	−1.7
s	—	—	—	—		0.22	4.7	1.9	8.4	1.2	3.4	6.3	2.6
n						7	12	12	12	12	10	10	10

[a] mean altitude, [b] Runoff/precipitation, [c] inorganic N, [d] after correction for unmeasured dry deposition.
[1] Crisp 1966, [2] Cryer 1976, [3] White et al. 1971, [4] Reid et al. 1981, [5] Edwards et al. 1984, [6] Hughes 1984, [7] Calculated from date including averages of several watersheds and several years: Avila & Rodà 1988, Bergstrom & Gustafson 1985, Escarre et al. 1984, Feller 1981, Feller 1987, Gosz 1980, Likens et al. 1977, Martin 1979, Paces 1985, Schindler et al. 1976, Sollins et al. 1980, Swank & Crossley 1987.

relatively rich in Ca^{2+}. The Ca^{2+} from these rains is probably retained within the soil exchange complex, which would increase the H^+ ion buffering capacity. Such rains may then play an important role in this area in compensating for acidic deposition inputs and nutrient outputs.

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