

Biogeochemistry of calcium in a broad-leaved forest ecosystem

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Abstract. This study of the biogeochemical cycle of Ca has been carried out in an oak-hornbeam forest ecosystem on a soil derived from the alteration of Famennian (upper Devonian) shales. The physical nature of the geologic substrate made it possible to use the watershed-ecosystem approach by monitoring the loss of Ca by streamflow. Input of hydrogen ions and Ca from rain were average as well as that of mineral nitrogen of which 50% was ammonium-N. Modelling the biogeochemical cycle of Ca in this ecosystem proved to be difficult owing to the heterogeneity of the geologic substrate.

The cationic denudation occurred mostly with bicarbonate ion as a carrier of the base cations towards the streamflow. Seasonal effects on streamwater cationic composition were in relation to maximal soil respiration occurring in the autumn. In addition to this effect, the electrolyte concentration of streamwater was determined by rain and by changes in concentration of the soil solution either by evapotranspiration or by freezing. In spite of widely fluctuating values of flow rate, the concentration of the streamflow remained constant within a factor of two or at the most three. The mechanism underlying this buffering action of the soil on the concentration of the solution flowing through it, was shown to be related to ion-exchange processes.

Introduction

Many forest ecosystems are losing calcium at the present time at a rate that may exceed the amount that can be extracted from calcium-bearing soil primary minerals by the normal weathering processes. This unbalance between input and output cannot have existed for centuries as demonstrated by Federer et al. (1989) on the basis of an extensive amount of information collected in the northeastern United States. Similar conclusions were drawn by Bonneau et al. (1991) from investigations of the coniferous forests in the Ardenne and Vosges regions of northeastern France. According to Ulrich (1991), acid deposition into the Sölling spruce forest has been accumulating continuously since the middle of the last century from a negligible amount in 1850 to the present catastrophic rate. By an ingenious backward extrapolation, he estimated that this excess acid pollution could weather the equivalent of 3 to 17 Mg CaCO₃ ha⁻¹.

There are two ways in which the consequences of this situation may be anticipated: either by establishing a balance between the inputs and outputs of Ca for the ecosystem or by a compartmental analysis of the Ca fluxes within, into and out of the ecosystem. From the latter approach, a set of

differential equations may be written that describe the fluxes and that can be used for simulating the probable evolution of the calcium balance during the next few centuries. Clearly the most difficult measurement is an estimate of the transformation of insoluble forms of calcium in the soil to the available forms: exchangeable, soluble or easily soluble.

Material and methods

The observations reported here were carried out in a forest of the Fagne de Chimay at 4°14'53" long. East and 50°06'51" lat. N. This forest is essentially composed of a stand of *Quercus* (predominantly *Q. robur* L.) with some *Quercus petraea* LIEBL. This stand dominates a coppice of hornbeam (*Carpinus betulus* L.) and comprises interspersed trees of other species such as: *Acer pseudoplatanus* L., *Fagus sylvatica* L., *Fraxinus excelsior* L., *Acer platanoides* L., *Acer campestre* L., *Alnus glutinosa* L., *Betula pendula* L. Roth., *Populus tremula* L., *Prunus avium* L., which forest management has maintained at a rather low proportion in keeping with a century-old practice of increasing the proportion of oak in the stand and favoring a form of 'coppice-with-standards'. A general description of this type of forest and of related types in the same region may be found in Noirfalise (1984), where the plant associations characteristic of the various facies are described as well as the ground vegetation typical of clearings.

Extensive investigations by Duvigneaud, Galoux and coworkers on a similar type of forest were carried out in Virelles-Blaimont near Chimay (less than 10 km of the present site) during the 1960s and have been reported in many different articles and book chapters. See for instance: Schnock (1967), Galoux et al. (1967), Duvigneaud (1984), Galoux (1978, 1983), Duvigneaud & Denayer-Desmet (1964, 1970), Reichle (1981, Stand No 28 and 29 of the IBP).

At that time, the potential of the watershed-ecosystem concept had not been fully realized, and the location of the earlier investigations on a limestone hill precluded any use of streamflow gauging to estimate the output from the ecosystem through streamflow. For this reason, the work reported here has focused on the watershed mass balance of this ecosystem rather than on repeating determinations carried out by the authors quoted above, unless for spot checking the similarities between the two ecosystems studied.

The soils of this forest have been described and mapped by Rémy (1981). The parent material is composed of Famennian shales (upper Devonian) which have weathered to a heavy clay covered by a rather thin humic layer of a mull to moder type. The soils may be classified as Dystrochrepts or 'sol brun forestier' with poorly developed profile differentiation except those due to reduction processes. They are shallow and the parent material or its

weathered product is always found close to the surface. Here and there, some small areas are covered with the remnants of a loessial Quaternary deposit, the depth of which never exceeds 0.5 m in the location of this study. The low permeability of the parent material or of its weathering products often causes the presence of a perched water table with the ensuing reduction processes. Most if not practically all the water circulation is by subsurface flow through the surficial organic or hemiorganic soil horizons. This causes the flow rate of the streams to have a pronounced rising hydrograph to precipitation.

Exchangeable cations in the soil were determined by displacing them with an excess of 1N ammonium acetate, filtering the solution through a Büchner funnel as described by Thomas (1982), evaporating the ammonium acetate solution to dryness, and treating the residue with nitric and perchloric acid in order to remove the small amounts of acetamide left after evaporation and to insolubilize silica, the acid solution was filtered off, the filtrate made to volume and concentrations of cations determined using atomic absorption spectrophotometry. The total amount of Ca, Mg, K and Na in the soil and in the parent material was determined after solubilization with HF and HClO₄.

The cation exchange capacity of the soil (0–10 cm) is about 13 cmol_c kg⁻¹. 20 to 40% of these negative charges are compensated by alkali and earth-alkali cations with a resulting pH of 5.4 to 6.5. Locally calcareous nodules influence soil pH and saturation of the cation exchange capacity.

The total amount of Ca found in the upper soil layer (0–10 cm) was 1.1 g kg⁻¹ in the soil sieved at 2 mm, while the Ca content in unweathered slate fragments was 0.66 to 1.05 g kg⁻¹.

The climate is characterized by a rather uniform distribution of rain with a yearly total slightly below 100 cm; the average annual air temperature is 8.4 °C with summer mean monthly maxima of about 20 °C and winter minima of -2 °C. As determined by Galoux et al. (1967), the growth period of the trees, i.e. between the average dates of half-leaving-out to half-leaf-fall, is about 155 days and approximatively equal to the number of days with an average air temperature ≥ 10 °C.

The hydrologic yield of the forest was calculated from the results obtained during the years 1985 to 1989, during which the total annual amounts of rain were 771, 960, 1073, 1146 and 854 mm, respectively. The daily measurement of streamflow was related to the area of the catchment. The total actual evapotranspiration was (in % of the incident precipitation): 62, 61, 54, 54, and 61 for the years indicated.

Rain was measured and analyzed at two sites less than 7 km apart; the measurements of precipitation made for the purpose of chemical analysis of rain agreed fairly well with those from a network for climatic observations at four other locations, with the exception of the amounts collected

during thunderstorms. The measurements of the chemical composition of rain were carried out during two years at the two locations. The dominant wind direction during the day rain was collected, was noted by means of a recording anemometer. Analyses were made immediately, i.e. on the day of collection, with respect to the concentrations of nitrate, ammonium, pH and total alkalinity. The rest of the sample was immediately frozen and kept for later determinations that were carried out by absorption spectrophotometry for the major cations (Ca, Mg, Na and K). The usual precautions were taken for avoiding interference during the atomic absorption spectrophotometry by adding LaCl_3 . The turbidimetric method (APHA 1981) was used for sulfate and a silver-silver chloride electrode for chloride. Specific ORION electrodes were used for the determinations of ammonium and nitrate nitrogen.

Since analytical chemistry of very dilute solution such as rain is not easy, standards establishing the accuracy and consistency of the results facilitate a comparison of our results to other laboratories. All results reported below have been checked according to the criteria presented by Campbell (1983) and McQuaker et al. (1983).

Losses of elements from the catchment studied are primarily determined by streamflow, which was measured with a V-notch weir. The streamflow estimates were checked episodically by the traditional salt dilution method (Schloesing 1863), the reliability of which has been confirmed recently (Okunishi 1992). The tracer used was sea salt (NaCl), the concentration of which was measured with a conductivity meter. The flow rate of the effluent was measured daily with the exception of a few days when the weir was totally frozen during the winter.

The chemical composition of the effluent was determined at least twice a week during two years. The frequency of sampling was determined by the flow rate – less frequent when the flow changed very little and more frequent when it changed rapidly (i.e. whenever a flood occurred).

Internal fluxes in forest ecosystems that can be fairly easily measured are the amount of litterfall and the amount and composition of the throughfall with respect to the incident precipitation. Litterfall was collected continuously in ten 1×1 m frames with 2-mm mesh bottoms from late August until late November. The frame contents were removed weekly, dried at 80°C before weighing, and aliquots were ground and dissolved in a mixture of nitric and perchloric acid. Throughfall was measured with 10 rain gauges spread randomly over 0.5 ha, the contents of the gauges were pooled and analyzed in the same way as rain water.

Table 1. Average composition (micromole^c L⁻¹) of stream water with standard errors of the means (on 252 samples).

Ca	1268(25)	Cl	400 (6)
Mg	423(8)	SO ₄ ⁻	335(7)
K	37(1)	NO ₃	90(5)
Na	373(6)	HCO ₃	1426(40)
Sum	2101(38)	Sum	2252(43)

Results

Chemistry of rain water and throughfall

The volume weighted average rain pH during two years (1985 to 1987) was 4.4 corresponding to a proton flux of 0.4 kEq. ha⁻¹ yr⁻¹. The annual input of Ca was 10.6 kg ha⁻¹ yr⁻¹ and the input of mineral N was 15 kg ha⁻¹ yr⁻¹, of which 49% was ammonium-N. Total sulfate brought in by rain was 34.8 kg ha⁻¹ yr⁻¹. Inputs of Na (7.9 kg ha⁻¹) and Cl (12.3 kg ha⁻¹) were significantly correlated which may be related to the relatively short distance (200 km) between the site and the sea.

The checks on the consistency of the chemical determinations of rain were made according to Campbell (1983) with the following results: deviations from electroneutrality amounted to an excess of positive charge of about 10% while the calculated electrical conductivity was equal $\leq 4\%$ of the measured value during the first year and 37% during the second year.

The origin of the precipitation and its acidic content is illustrated by Fig. 1 consisting of compass roses, the spokes of which are proportional to the amount of hydrogen ions or of rain brought in from the corresponding azimuth. Most of the rain originated from the southwestern sector, as usual in this part of Europe. The amount of hydrogen ions may follow a similar pattern (Fig. 1A) or deviate markedly from it (Fig. 1B).

Stream water chemistry and nutrients output

The average composition of stream water is illustrated in Table 1 which summarizes the values of 221 samples together with the standard errors of the means. The electroneutrality was almost exact and improved slightly when speciation of the solution was corrected by a speciation programme such as GEOCHEM (Sposito & Mattigod 1983; Sposito 1986) which does not demand electroneutrality of the input data and allows the calculation of the concentration of complexes or precipitates. Ion pairs formed in non-negligible

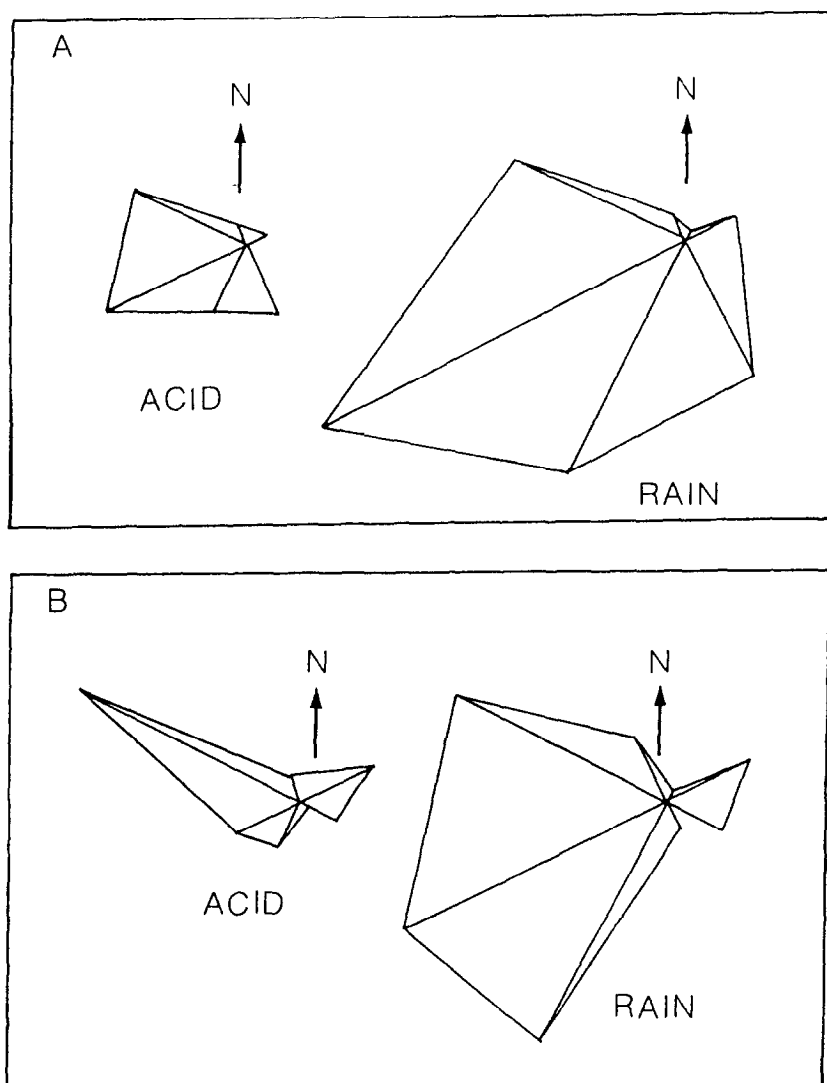


Fig. 1. Compass rose for the amounts of hydrogen ions deposition and rain brought in from the indicated azimuth for observations made near the Forest Research Centre of the Fagne de Chimay. (A) from July 1985 to July 1986. (B) from July 1986 to July 1987.

proportions were $\text{CaSO}_4^{(o)}$, $\text{CaHCO}_3^{(+)}$ and $\text{MgSO}_4^{(o)}$ which amounted to 13.8, 8.5 and $3.8 \mu\text{mole l}^{-1}$, respectively. It may be noted that the absence of any anion deficit points to a negligible concentration of dissolved organic carbon.

Average pH resulting from 622 measurements of streamwater carried out during ten years was 7.47. The average alkalinity was $1.45 \text{ mmol}_c \text{ L}^{-1}$, so the average partial pressure of CO_2 to which stream water had been exposed

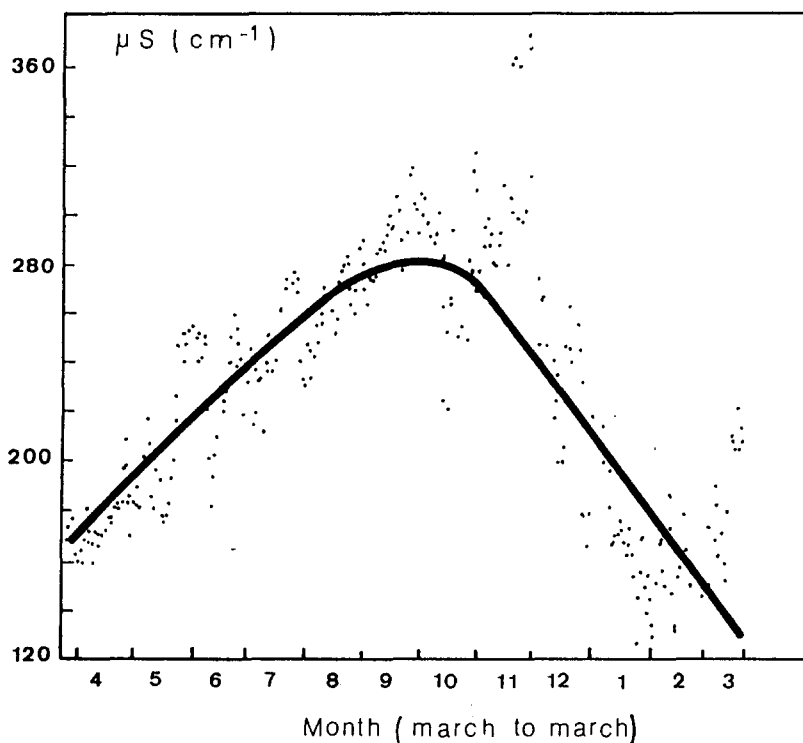


Fig. 2. Average value of the conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$) of the streamflow between 1979 and 1989 for day of the year starting on March 23 irrespective of the calendar year.

during its subsurface flow, was at least 0.003 (i.e. roughly ten times the partial pressure of CO_2 in the atmosphere). Appreciable fluctuations around this value have been demonstrated by Laudelout (1985) and interpreted as due to the seasonal peaks of microbial activity in these soils (Laudelout & Lambert 1982).

Seasonal effects on the electrolyte concentration in streamflow are illustrated by Fig. 2, which is based on a large number of electrical conductivity values. The latter can be used a reliable index of total electrolyte content since the ratio of conductivity to ionic concentrations was almost constant, activity effects being negligible at the concentrations reported (Table 1). In Fig. 2, the electrical conductivity of stream water has been plotted vs day of the year starting on March 23rd for 365 days. These data comprise about 600 measurements of electrical conductivity carried out during 10 years from 1979 to 1989 at irregular intervals. For any given day of the year, 0, 1, 2 or at the most 3 measurements were obtained, the day average was calculated, after which a moving average between three successive days was calculated from the day averages. The smoothing method used for obtaining the curve of Fig.

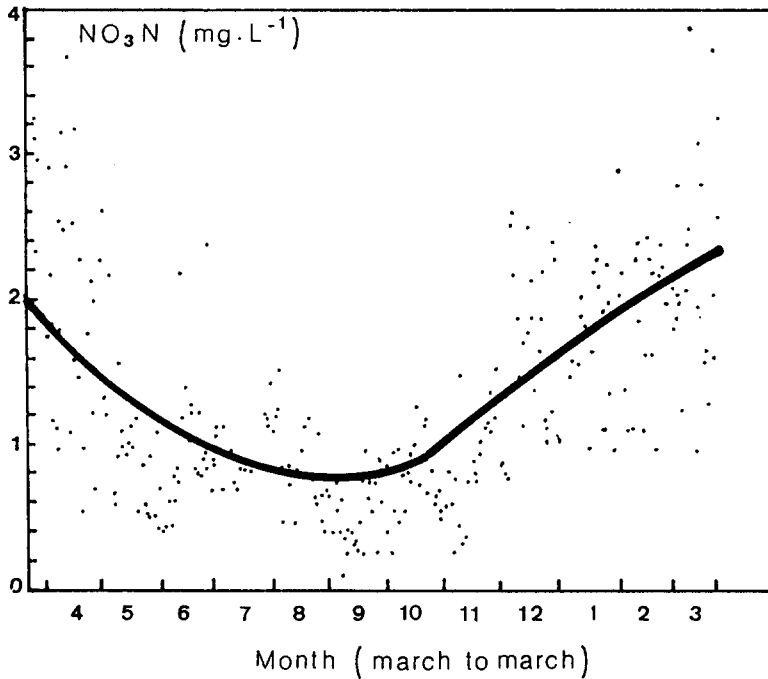


Fig. 3. Values of the nitrate content of the streamflow between 1982 and 1989 averaged and smoothed as above.

2 was the Locally Weighted Regression scatter plot Smoothing (LOWESS) which is quite convenient for fitting a curve to a set of points in a scatter plot (see Chambers et al. 1983). A rather obvious trend is apparent: electrolyte concentration in the effluent increased from late March reaching a maximum during the autumn and decreasing during the winter. The seasonal variation observed for the total electrolyte content was reflected by that of the main ionic constituents of the streamflow, namely Ca^{++} and HCO_3^- as shown by the boxplots of Fig. 4, in which the observed range of concentrations is apparent. This pattern coincided with the onset of growth of the herbaceous plant cover in early spring, and it is inverse to the distribution found for nitrate concentration (Fig. 3).

The concentration range of Ca^{++} and HCO_3^- is much smaller than that for the variation in flow rate, which can extend over several orders of magnitude. Within a limited range of flow rates, as shown by Fig. 5, a buffering effect on streamflow concentration becomes apparent when conductivity of the effluent is plotted with respect to streamflow. Up to 8 mm day^{-1} , a significant linear relationship could be fitted to the data of Fig. 5:

$$\text{Conductivity}(\mu\text{S.m}^{-1}) = 201 - (7.55 \pm 1.99) * \text{Streamflow}$$

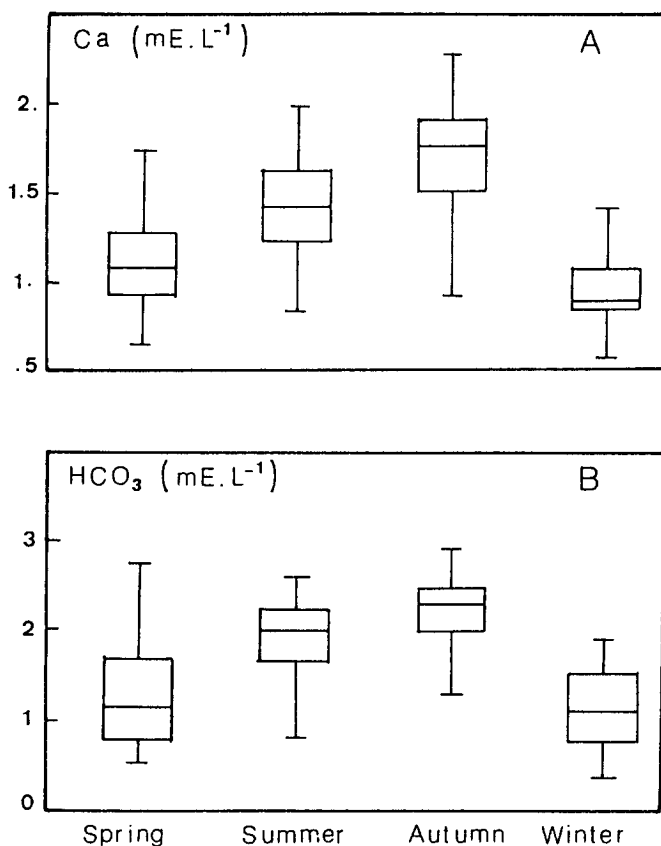


Fig. 4. Boxplots of Ca^{++} and HCO_3^- concentrations in streamflow according to season.

An intercept of 201 was found by this regression instead of 230 found for the grand average of all conductivity values. The low value of the slope of the regression points to the efficient buffering of the electrolyte concentration against the dilution caused by the increased flow rate. The possible effect of ion exchange processes in buffering the concentration of the effluent against flow rate was investigated by tracing the evolution of the ratio of divalent to monovalent base cations with increasing dilution of the streamflow. This is shown by Fig. 6 in which the ratio of the concentrations, expressed in $\text{cmol}_e \text{ l}^{-1}$:

$$\text{M}^{++}/\text{M}^+ = (\text{Ca} + \text{Mg})/(\text{Na} + \text{K})$$

has been plotted vs streamflow (mm day^{-1}). The slope of the straight line relationship fitted to the data was -0.14 ± 0.003 while the intercept had the value of 3.75 ± 0.06 . The value of this intercept may again be compared to

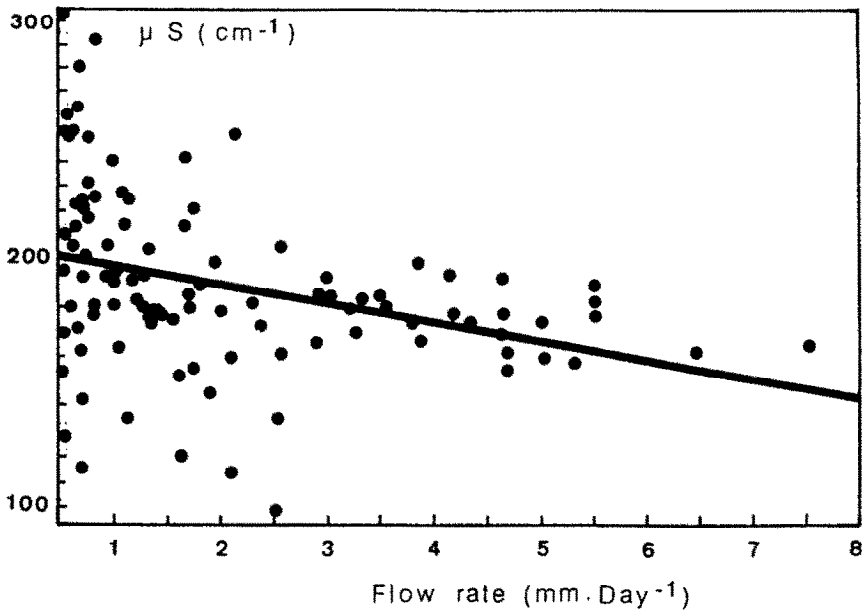


Fig. 5. Change of the electrical conductivity of streamflow ($\mu\text{S}.\text{cm}^{-1}$) with flow rate in ($\text{mm}.\text{day}^{-1}$) at values higher than $0.5 \text{ mm}.\text{day}^{-1}$.

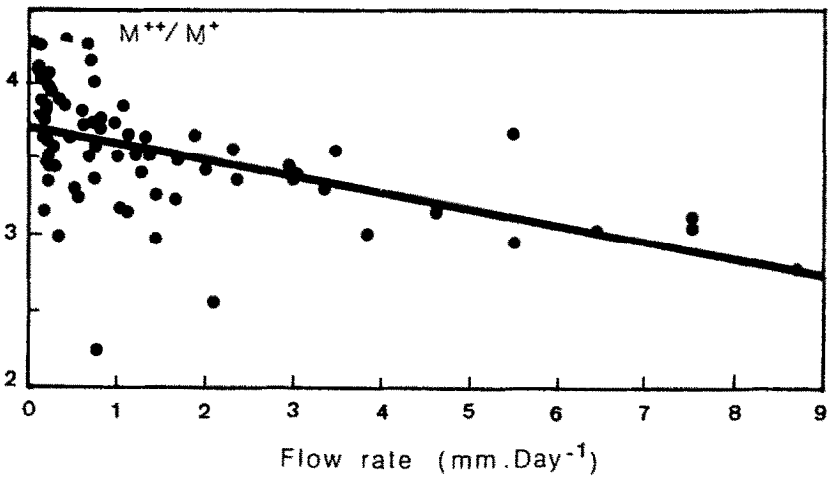


Fig. 6. Change of the divalent to monovalent base cation ration in streamflow with flow rate.

the values of the $\text{M}^{++}/\text{M}^{+}$ ratio of base cations from the grand average of all determinations of base cations concentrations in the streamwater, i.e. 4.1 (Table 1).

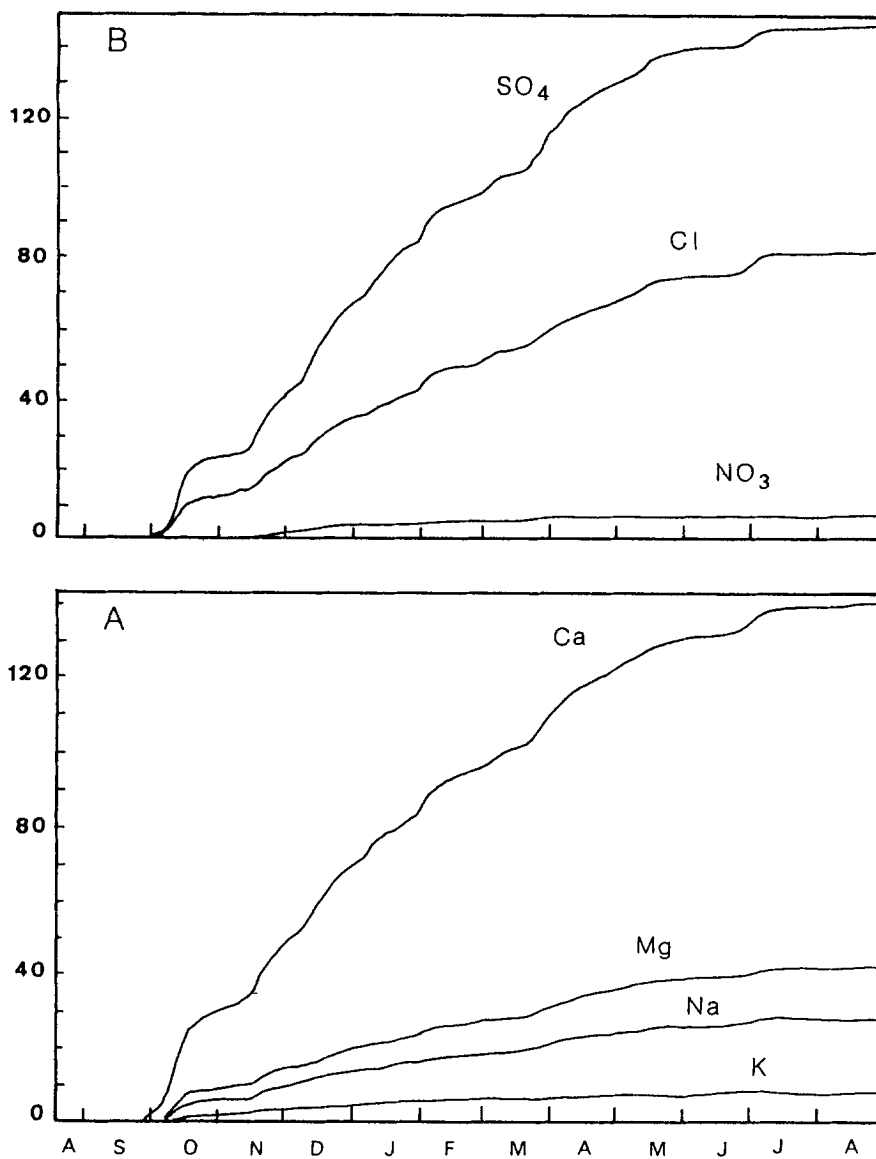


Fig. 7. Output of cations (A) and anions (B) in $\text{kg yr}^{-1} \text{ ha}^{-1}$ during the year 1982-1983. The curve has been centered on Jan. 1 1983.

The main difficulty in interpreting this type of relationship is caused by the interplay of purely chemical factors such as the effect of dilution on processes of ion exchange, ion exchange hydrolysis or ion exchange chromatography.

Output of nutrients from the ecosystem

Output of nutrients has been calculated by multiplying the flow rate by the observed concentration of the elements and relating the output to the area of the catchment (400 ha). The results are depicted in Fig. 7A and B as the cumulative removal in kg element per ha during the year 1982–83. The figures have been centered on January since most of the losses occur 3 to 4 months before and after that month. Output from the ecosystem slows considerably after the onset of growth of the trees in May until its cessation in October. This was due to a strongly increased uptake of minerals by the plant cover and a decreased flow rate, caused not so much by decreased precipitation as by increased evapotranspiration.

On a weight basis the losses of Ca by streamflow exceeded those of the three other elements and amounted to $140 \text{ kg ha}^{-1} \text{ yr}^{-1}$. It may be noted that a good estimate of Ca losses by streamflow could have been approximated by using the yearly average of rain and measured streamflow combined with the average of Ca concentration in streamflow i.e. for five successive years. The total rainfall was 4.8 m, of which 2.8 m was lost by streamflow yielding a five-year loss of 562 kg, or a yearly average of 112 kg, close to the actual measurement. Taking account of the atmospheric Ca input, a round figure of $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$ may be accepted for the loss of Ca by the ecosystem.

Cations cannot be removed from an ecosystem if they are not accompanied by an equivalent amount of anions so that electroneutrality is maintained at all times. The major anion carrier for Ca^{++} is bicarbonate which balances two-thirds of the Ca lost from the ecosystem. This is apparent in Fig. 4 and also from the strong correlation between Ca^{++} and HCO_3^- concentrations in the effluent which is expressed by the following regression line:

$$C_{\text{Ca}} = 0.48 + 0.57C_{\text{HCO}_3} (R^2 = 0.84)$$

and between the sum of cation concentrations:

$$C_{\text{S}+} = (\text{Ca} + \text{Mg} + \text{K} + \text{Na})$$

and bicarbonate concentration:

$$C_{\text{S}+} = 0.83 + 0.89C_{\text{HCO}_3} (R^2 = 0.86)$$

Suspended matter. A number of determination of suspended matter in the stream water gave an average of 23.6 mg L^{-1} dry matter with a high of 67 and a low of 4.5. These low values are understandable given the low value of the slope and the high value of the tortuosity of this forest stream as demonstrated by Legrand & Laudelout (1985).

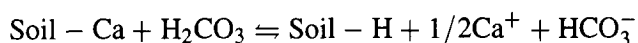
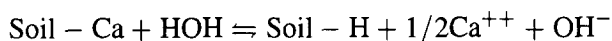
Discussion

Processes in the soil as mirrored by streamflow composition

Changes in the concentration of the soil solution are mirrored by streamflow. Dilution of the soil solution by rain is immediately reflected in streamflow concentration – albeit with a considerable buffering of the concentration change as evidenced by Fig. 5, which shows the slow decrease of electrolyte concentration with increasing streamflow.

The buffering of the soil solution concentration very likely occurs through ion exchange processes while the soil solution seeps through the upper horizons in subsurface flow. This is evidenced by the immediate response of the ratio of divalent to monovalent base cations to dilution as evidenced by the change to this ratio with streamflow as shown by Fig. 6. In any heterovalent exchange reaction, diluting the equilibrium solution will enhance the ratio of adsorbed divalent to monovalent base cation and consequently decrease that ratio in the solution. This may be considered as a consequence of the Le Chatelier moderation principle: dilution of the soil solution is opposed by the liberation of monovalent cations into it and consequently a decrease in the ratio of divalent to monovalent cations in the solution.

Ion exchange reactions that may be considered as responsible for cationic denudation of the soil are the following:



Since these reactions progress to the right by the irreversible transformations of the hydrogen-clay, the exchange may proceed indefinitely and is actually irreversible unless special precautions are taken for avoiding lattice dissolution by protons as shown by Gilbert & Laudelout (1965).

Table 2 shows a comparison of the cationic composition of stream water, with that of the exchangeable cations in the upper layers of the soil and that of the litterfall from the vegetation. The similarity in composition is quite apparent with the exception of a reversal of the proportion of Na to K in the stream water, caused by preferential uptake of K by the plant cover.

It was to be expected that the concentration maximum of streamflow would coincide with the period of maximum evapotranspiration. However, as shown by Figs. 2 and 4, the concentration maximum is shifted towards the autumn period. One of the factors responsible for this effect could be the greatly enhanced soil respiration during this period (Laudelout & Lambert 1982; Laudelout 1985). Figure 4 shows that the concentration of the HCO_3^- carrier anion is indeed enhanced in the autumn, which allows for its greater role as a cation carrier in the process of chemical denudation.

Table 2. Cationic composition of four compartments in the ecosystem (the first 4 columns in % of the content in col 5 expressed in the units presented in col 6, the last column contains the ratio of divalent to monovalent cations).

	Ca	Mg	Na	K	Content	Units	M^{++}/M^{+}
Litterfall	66	16	3	15	0.86	$\text{cmole}_c \text{ g}^{-1}$	4.5
Exch. cations	68	19	5	8	3.5	$\text{cmole}_c \text{ kg}^{-1}$	6.7
Stream water	60	20	18	2	2.2	$\text{mmol}_c \text{ L}^{-1}$	4.0
Soil solution	50	13	20	17	1.49	$\text{mmol}_c \text{ L}^{-1}$	1.7

For an anion such as nitrate, uptake by plants overshadows the effect of other factors such as increasing concentration or enhanced biological production during the summer months. The result is a minimum of nitrate concentration during the summer: a fact which is in parallel with the retentive capacity of the ecosystem with respect to mineral N: from the 15 kg mineral N reaching the ecosystem yearly as wet and dry deposition only 7 kg are lost in streamflow. This amount was measured (Fig. 7), but it could also have been calculated from the grand average of $\text{NO}_3\text{-N}$ content in streamflow (i.e. 1.4 ppm) and the fraction of the total precipitation that reached stream flow during the five-year study quoted above.

Compartmental analysis of the fluxes in the ecosystem

A further interpretation of the processes occurring in the ecosystem may be made by integrating the flows of Ca between its compartments. The definition of these compartments is essentially conceptual as shown by Fig. 8, which is admittedly a simplified representation of the Ca cycle. The structure chosen is similar to the model used by Waide et al. (1974) and to some extent to that of Bonneau et al. (1991) for the biogeochemical cycle of calcium in a forest ecosystem; a rather similar scheme has also been used by Johnson (1992). This scheme is probably the simplest that can be elaborated and still may have some predictive value. Some discrepancies between the schemes quoted above and the one presented here consist in partitioning the precipitation input between canopy and litter or in neglecting the rejuvenation of the soil profile by erosion.

The model is essentially made up of a loop between 3 compartments, i.e. from the pool of available Ca to vegetation to litter and back. There are two main inputs: Ca in precipitation and Ca from the weathering of Ca-bearing minerals in soil and parent material; the most important loss is by streamflow and in the case of this oak forest, a comparatively minor one by logging.

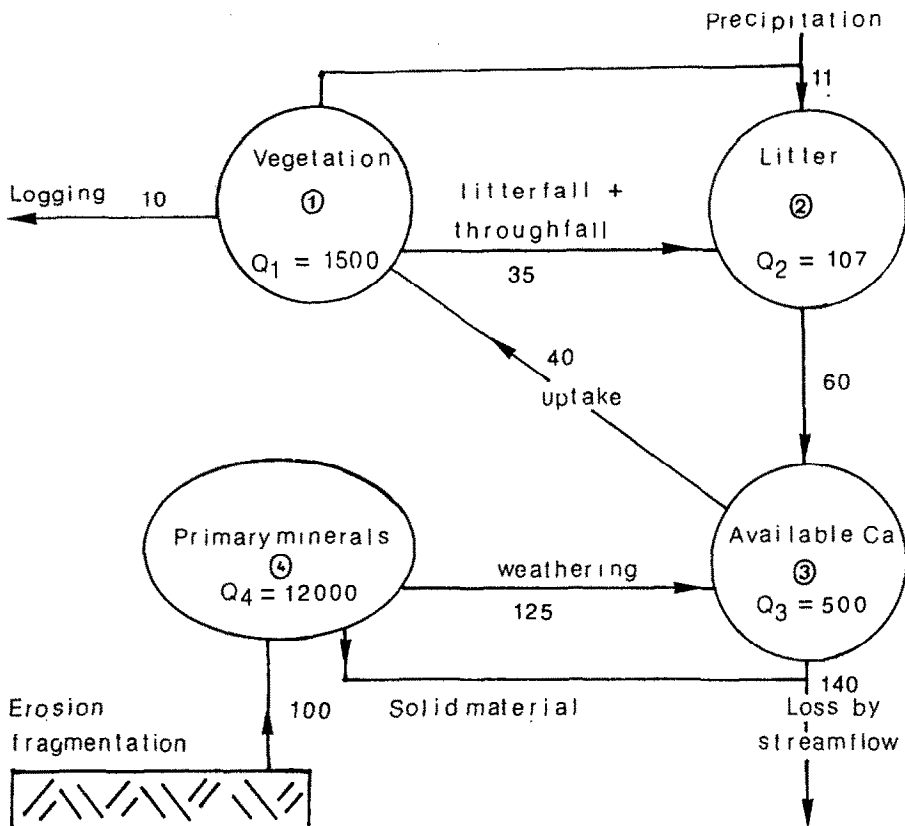


Fig. 8. Compartmental scheme used for modelling the biogeochemical cycle of calcium in the ecosystem, the figures for the compartment contents or fluxes between them are discussed in the text.

From the content of these compartments and the fluxes between them, first-order constants may be calculated under the assumption that the behavior of the system is linear. The latter condition is expressed by:

$$k_{ij} = F_{ij}Q_j$$

where Q_j is the content of compartment j , F_{ij} is the flux from compartment j to i , k_{ij} is the first order constant thereby defined and which may be estimated from the measured values of F_{ij} and Q_j at any given time. A full discussion of linear ecosystem analysis may be found in Waide et al. (1974, p 341 ff). Once the rate constants are known, the model of Fig. 8 may be translated into a set of ordinary differential equations, the numerical solutions of which may be easily obtained by, e.g. a Runge-Kutta method of the fourth order, (a BASIC program is available upon request).

The differential equations are written by expressing the rate of change for the contents of the four compartments defined by Fig. 8 as follows: for compartment 1: (plant material) its content Q_1 changes with time according to the algebraic sum of the following terms: (i) Uptake from the pool of available Ca which is considered to be linearly proportional to the content of compartment (3). The proportionality constant is calculated from the measured flux F_{13} and the initial content Q_3 . (ii) Litterfall and throughfall towards forest litter. (iii) Loss from logging: L_1 . This translates as:

$$\frac{dQ_1}{dt} = k_{13}Q_3 - L_1 - k_{21}Q_1$$

An identical procedure is followed for the rate of change of compartment (2) giving:

$$\frac{dQ_2}{dt} = k_{21}Q_1 - k_{32}Q_2 + I_1$$

Calcium input I_1 to the litter by rain is added to litterfall enhanced by amount of Ca in throughfall.

In compartment (3), output towards the streamflow is set equal to the measured flow divided by the initial Ca content times the compartment content. Input will be set equal to the sum of the fluxes from (2): $F_{32} = k_{32}Q_2$ and to that from (4) i.e. $F_{34} = k_{34}Q_4$, this gives:

$$\frac{dQ_3}{dt} = -k_{13}Q_3 - k_{32}Q_2 + k_{34}Q_4$$

Finally the fourth compartment, containing unweathered or partially weathered Ca-bearing minerals loses an insignificant amount of solid material in streamflow and provides by weathering replacement of lost Ca in compartment 3. Replenishment of compartment 4 occurs through rejuvenation of the soil profile.

Implementation of the model requires that an estimate be made for contents of the compartments and of the fluxes between them.

Estimates of the Ca content of the four compartments

The amount of Ca contained in the four compartments may be approximated as follows: a reasonable estimate of the amounts of Ca in trees may be obtained from the basal area in the ecosystem which is now about 25 m²/ha with extremes of 15 and 30 m² ha⁻¹. Given the mineral content of the common species, as tabulated by Duvigneaud (1984), a stand volume of about 250 m³ would correspond to about 1500 kg ha⁻¹ of Ca. From our measurements and

those of Duvigneaud & Denayer-Desmet (1964, 1970), the Ca content of the litter is about 100 Kg ha^{-1} . The amount of available Ca may be approximated by 500 Kg ha^{-1} and that of total Ca by $12,000 \text{ Kg ha}^{-1}$. The last two figures are derived from our measurements of the Ca concentrations in the soil and the parent material and from an assumption regarding the depth of the soil from which Ca can be weathered or the depth of the soil from which it can be absorbed or leached, namely 0.2 and 1.0 m.

Inputs of Ca

The amount of Ca brought in by precipitation is $11 \text{ Kg ha}^{-1} \text{ yr}^{-1}$ which is distributed between canopy and litter. For simplifying matters, it will not be apportioned between these two compartments in the model, and it is attributed to the litter to which most of it comes down eventually, especially in the winter months. It has been shown by Denayer-Desmet (1969) that stemflow in this type of forest is negligible.

Calculating the amount of Ca brought in by weathering is difficult. An estimate could be obtained by a method which has been described by Barth (1961) and utilized by Johnson et al. (1968) and more recently by Wakatsuki & Rasyidin (1992). The basis of this calculation is as follows: at steady-state the weathering rate of the rock or partially weathered material W_r may be expressed by:

$$W_r = \frac{F_i}{C_i - s_i}$$

where F_i is the net amount removed by streamflow per unit time, while C_i and s_i refer to the concentration in the soil and in the parent material. This can hardly be applied to the biogenic elements Ca, Mg and K since cycling by vegetation results in total concentrations in the soil that are higher than in the unweathered material. However, when the physiological role of an element is minor, as in the case of Na, the amount lost by stream flow is $24 \text{ kg ha}^{-1} \text{ yr}^{-1}$, and the input of Na from atmospheric precipitation is 7.9, then the net rate of loss is 17.1. The concentration of total Na in the soil is 7.0 g kg^{-1} and an average of 12.5 g kg^{-1} in the unweathered material, so an approximate weathering rate of the parent material could be:

$$W_{Na} = \frac{17.1}{12.5 - 7.0}$$

i.e. a weathering rate of about $3 \text{ kg ha}^{-1} \text{ yr}^{-1}$ of the parent material. This would provide a negligible quantity of Ca by weathering to compensate for the loss by streamflow. Clearly, either the latter is greatly exaggerated, which

is unlikely, or the result of the calculation of the extent of weathering is a gross underestimate. As noted by Miller et al. (1993) for a montane ecosystem, if the entire cation loss were derived from the exchangeable cations pool, it would be exhausted after a few years, in our case, five years would be sufficient to exhaust it entirely. The most likely explanation of the high amount of Ca exported by streamflow is that part of the seepage below the organic horizons flows locally on some slate strata containing calcareous nodules mainly in the headwaters of some tributaries where deeper incision of the landscape has led to uncovering these strata wherever they were present. For this reason, the flux of Ca is much larger than the overall content of Ca in the soil and the parent material would lead one to estimate. Above all, as noted by Miller et al. (1993) for a spruce-fir ecosystem, if the entire cation loss were derived from the pool of exchangeable Ca, the latter would be exhausted after very few years; in this case, only five years would suffice.

The value of the weathering flux is the only parameter in the scheme of Fig. 8 for which there is no measured data or reasonable estimates. Use of the model may be considered as a method for determining one parameter from the other parameters which are known. The estimate of the unknown flux must be made in such a way that some continuity in the evolution of the ecosystem be maintained. This yields an amount of 100 Kg Ca liberated not only from the bulk parent material but also from the local concentrations of calcareous nodules. In that case, a better balance of the Ca budget of the ecosystem is obtained and the numerical solution remains stable.

Outputs from the ecosystem

As shown above, the output by streamflow is estimated to be about 120 to 140 Kg ha⁻¹ yr⁻¹. The mean annual Ca export from the forest ecosystem by logging may be estimated from the data collected by the Forest Administration in Chimay during this century and earlier from 1549 to 1789 by the seigniorial administration. Logging has removed an average of one to three m³ per ha per year in the course of several centuries, the corresponding Ca losses may be estimated at 10 kg ha⁻¹ yr⁻¹.

Internal fluxes

Among these fluxes, the amount of Ca returned yearly to the soil by litterfall is fairly easy to estimate from the measurement of the amount of litterfall and of its Ca content. This was done during two successive years at two sites and gave results very similar to those that have been obtained many times in temperate forest ecosystems since the early studies of Ebermayer (1876) and reviewed in details by Bray & Gorham (1964). The dry weight at site 1 was 2.50 Mg ha⁻¹ ± 0.24 and the next year 2.73 ± 0.51 Mg ha⁻¹ while the

corresponding values at site 2 were $3.25 \pm 0.65 \text{ Mg ha}^{-1}$ and $3.40 \pm 0.59 \text{ Mg ha}^{-1}$. The amount of Ca involved was $35 \text{ Kg Ca ha}^{-1} \text{ yr}^{-1}$, while in the Hubbard Brook Forest in New Hampshire, USA, the value was 41 (Likens et al. 1977; Driscoll et al. 1992), in spite of the widely different nature of the substrate.

The flux from the pool of available Ca for vegetation was estimated at 76 to $128 \text{ Kg ha}^{-1} \text{ yr}^{-1}$ by Duvigneaud & Denayer-Desmet (1970) on a much more calcareous substrate; a much lower value has been proposed for the Hubbard Brook forest by Driscoll et al. (1992). We have assumed $40 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for that value, taking account of the less calcareous nature of the substrate in comparison with that of the ecosystem studied by Duvigneaud and Denayer-Desmet. The flux from the litter to the pool of available Ca has been estimated at $60 \text{ Kg ha}^{-1} \text{ yr}^{-1}$ in accordance with the measurement of Duvigneaud & Denayer-Desmet (1964, 1970).

Introducing the numerical values listed above into the set of four ordinary differential equations did provide a rather stable behaviour of the model i.e. a non-oscillating numerical solution with a smooth transition from the present situation to a somewhat impoverished state, provided the value quoted above for the flux of Ca towards the pool of exchangeable Ca from the soil and parent material. Without going into a detailed report of the results of the simulation, it may be mentioned that after 300 years the amount of Ca in the vegetation decreased by a third while the pool of available Ca and consequently the losses of Ca by streamflow were reduced by a fourth.

Admittedly, the stability of the model was acquired at the cost of a rather peremptory assignment of the values of the fluxes from the weathering of Ca-bearing material and its reconstitution by erosion.

Conclusion

From the data presented above, it is difficult to conclude with some amount of certainty, whether the present loss of Ca by the ecosystem can be sustained during the next few centuries. The main difficulty arises from estimating the contribution of the parent material to Ca loss by reason of the large spatial heterogeneity of the distribution of main source of Ca to streamflow. In this case, the well-known difficulty of evaluating the weathering of Ca-bearing minerals has been shifted towards the evaluation of local rejuvenation of the substrate by incision of the landscape in the headwaters of the tributaries. The latter process while allowing considerable outflow will do little to rebuild the concentration of Ca-bearing minerals in the soil, so that conditions may be reached that will cause a decreased level of forest productivity.

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