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Variations of bioavailable Sr concentration and $^{87}Sr/^{86}Sr$ ratio in boreal forest ecosystems
Role of biocycling, mineral weathering and depth of root uptake

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Abstract. The mean depth of Sr and water uptake in mixed Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*) stands was investigated, using natural variations of $^{87}Sr/^{86}Sr$ and $^{18}O/^{16}O$ in soils in relation to depth. Three spruce-pine pairs were studied on a podzol and a peat site in Northern Sweden. Tree leaf and wood, as well as soils, soil solutions and roots below each tree were analysed for Sr and Ca concentrations and $^{87}Sr/^{86}Sr$ ratio. The $^{18}O/^{16}O$ ratio was also determined in xylem sap and soil solutions in relation to depth. Soil solution $^{18}O/^{16}O$ decreased in relation to depth. Comparing with xylem sap $^{18}O/^{16}O$ data indicated a deeper uptake of soil water by pine than spruce on the podzol site and a superficial uptake by both species on the peat. The $^{87}Sr/^{86}Sr$ ratio of bioavailable Sr generally increased in soils in relation to depth. Contrastingly, the $^{87}Sr/^{86}Sr$ ratio in spruce wood was generally higher than in pine wood suggesting a deeper uptake of Sr by spruce. But the $^{87}Sr/^{86}Sr$ ratio and concentrations of bioavailable Sr were systematically higher below spruce than below pine. In order to explain these unexpected results, we built a simple flux model to investigate the possible effects of interspecific variations in Sr cycling, soil mineral weathering and depth of Sr uptake on soil and tree $^{87}Sr/^{86}Sr$ ratio. At the study sites, spruce cycled in litterfall up to 12 times more strontium than pine. The use of the model showed that this difference in Sr cycling could alone explain higher isotopic signatures of trees and topsoils below spruce. Besides, high isotopic signatures of roots in the A/E horizons below spruce led us to hypothesise a species-specific weathering process. Finally, the comparison between the $^{87}Sr/^{86}Sr$ ratios in wood and root or soil solutions below each species suggested that the average depth of Sr and water uptake were close, but irregular variations of the Sr isotopic ratio with depth reduce the accuracy of the results. Tree species strongly influence Sr isotopic ratios in boreal forest soils through differences in Sr cycling, and possibly through specific mineral weathering.

Introduction

Base cations are supplied to forest ecosystems from two primary sources: atmospheric deposition and weathering of soil minerals. Many studies have attempted to quantify these two sources, because the sustainability of forest ecosystem fertility depends on these fluxes (see for instance Johnson and Lindberg (1992)). At some sites, the $^{87}Sr/^{86}Sr$ ratio of the Strontium (Sr) deposited from the atmosphere and released by weathering differ. The $^{87}Sr/^{86}Sr$ ratio of atmospheric deposition is mostly influenced by the $^{87}Sr/^{86}Sr$ ratio of the ocean. In Sweden the atmospheric $^{87}Sr/^{86}Sr$ ratio varies between 0.709–0.716 (Wickman 1996). The $^{87}Sr/^{86}Sr$ ratio of rocks varies according to their age and their original content of Rb and Sr (Faure 1986) because ^{87}Sr derives from the radioactive decay of naturally occurring ^{87}Rb (half-life 4.88 10^{10} years). As there is no isotopic fractionation during chemical and biological processes, this isotopic difference can be used to track Sr origin (Graustein and Armstrong 1983; Graustein 1989; Åberg 1995). Because rain Sr is deposited on the soil surface, whereas soil weathering releases Sr from mineral horizons, the Sr isotopic ratio may form a depth gradient. The relation between the tree and soil bioavailable Sr isotopic ratios may then be used to measure the mean depth and sources of Sr uptake (Wickman and Jacks 1993; Dambrine et al. 1997). As the chemical structure of Sr is close to that of Ca, the use of Sr isotopes to quantify Ca fluxes in forest have been developed in a number of recent studies (see the review by Capo et al. (1998)). The method, however, is associated with several inconveniences. Among these is the difficulty of measuring the isotopic ratio of the Sr released by weathering (Wickman and Jacks 1992; Bain and Bacon 1994; Bullen et al. 1997), as well as the likelihood that Ca and Sr cycling in soils and plants may differ (Elias et al. 1982; Poszwa et al. 2000).

In an earlier study in Northern Sweden, Bishop and Dambrine (1995) used the gradient of decreasing $^{18}O/^{16}O$ ratio in soil water with depth and compared it to the $^{18}O/^{16}O$ ratio of tree xylem sap to ascertain the mean depth of water absorption by different tree species growing in a mixed stand. Results showed that water uptake by Pinus sylvestris roots was on average deeper than that by Picea abies roots. This confirmed earlier speculations based on root density profiles. In this study, on a nearby stand within the same catchment, we investigated the mean depth of Sr and water uptake in order to determine whether water and Ca uptake patterns were similar. This issue is interesting to tree physiologists and critical for many soil cycling and acidification models in explaining the development of base saturation with soil depth. We hypothesised an increase of the $^{87}Sr/^{86}Sr$ ratio of bioavailable Sr with soil depth (Wickman 1996; Dambrine et al. 1997) given the age and nature of the parent material. Two sites were investigated, a mid-slope podzol on till, and a peat soil further down that slope. These soil types are the most common in boreal forests. We measured the Ca and Sr content and the $^{87}Sr/^{86}Sr$ ratio of spruce and pine sap wood and soils in relation to depth. A simple model of Sr circulation was built (1) to understand which processes controlled the observed $^{87}Sr/^{86}Sr$ ratio variations in trees and soils and (2) to estimate the mean depth of Sr uptake by spruce and pine. Soil water and tree xylem sap $^{18}O/^{16}O$ ratios were also measured to compare the mean depth of Sr and water absorption by the two species.

Materials and methods

General situation

The small (50 ha) Svartberget-Nyänget experimental catchment is located in the northern part of Sweden (62°14′N, 19°46′E), 55 km north-west from the city of Umeå on the Gulf of Bothnia. The elevation varies between 235 and 310 meters. The mean annual air temperature during the last decade was 1.1 °C with an annual precipitation of 600 mm, about 40% of which fell as snow. The growing season begins in May and ends in September. The deposition chemistry is characterised by a relatively low deposition of sulphur and nitrogen and a small degree of marine influence. The mean wet deposition for the period 1986–1989 was 6 kg S ha^{-1} yr^{-1} and 4.7 kg N ha^{-1} yr^{-1} with a very low dry deposition (Grip and Bishop 1990). Since then, deposition of S and N has declined by ca 50% (Bishop et al. 2000). Streamwater flows southwards from an 8 ha open mire through a small, ditched creek surrounded by till ridges. Average annual runoff has been 300 mm.

Pure Scots pine (*Pinus sylvestris*) stands cover the till slopes of the catchment and small patches of the mire. Pine is mixed with Norway spruce (*Picea abies* karst L.) and birch (*Betula sp*) in the lower part of the slopes. The field layer consists mainly of dwarf shrubs (especially *Calluna vulgaris, Vaccinium myrtillus, Vacc. vitis-idaea*) with a bottom layer of mesic mosses (*Pleurozium schreberi* and *Hylocomium splendens*) on the slopes. *Sphagnum* (spp) covers the mire and the soil in the band of peat along the stream.

The bedrock is characterised by veined gneisses of the proterozoic period (1880 Ma) with minor dykes of metamorphosed ultrabasic rocks. There is a shift to inland granites further North and West (10–30 km). This bedrock is overlain by locally-derived glacial till on the slopes and fluvioglacial sediments in the lower part (Ivarsson and Johnson 1988). The bulk mineralogical composition of the till is strongly influenced by the variability of the bedrock composition and the dominant rock types. Soils types are podzol on well drained slopes and peat in the lower areas of the catchment, often adjacent to the stream. The stream draining the mire and an ephemeral tributary west of the stream, were deepened and straightened ca 1920 in order to improve the growth of the forest on the peat soils which were grazed during the 1800's and early 1900's.

Study sites

Two sites were chosen about 50 meters from the site originally studied by Bishop and Dambrine (1995). At both of the new sites (as at the original site), there was a mixed stand of spruce and pine of about the same size. The new sites differed with respect to their drainage.

The Sva 1 podzol site is similar to the original site, located mid slope on the till. The soil is a well-drained podzol, with a sandy texture, and rich in boulders throughout the whole profile. The humus layer is a mor with an average thickness of 5 cm and distinct L, F and H layers. A dark organo-mineral A layer sometimes appears as a transition between the H horizon, and the bleached E layer. The combined thickness of the E and A horizons averages 15 cm. The Bh horizon is irregular, but about 5 cm thick. The spodic Bs horizon is well developed and ca 20 cm thick. Transitions between the Bh, BC and C horizons are diffuse. The micromorphology, mineralogy and chemistry of a podzol profile, referred to as Nyänget, located on the upper slope of this catchment, has been studied in detail by a team of soil scientists (Lundstrom et al. 2000). After Olsson and Melkerud (2000), soil weatherable primary minerals in the BC horizon are biotite (2%), hornblende (4.1%), plagioclase (3.6%), alkali-feldspar (18.4%), and muscovite (0.8%), among which plagioclase and biotite are the most weathered. The degree of weathering of most minerals slightly increased from the BC to the Bs except for hornblende, the abundance of which strongly decreased to 2.8%. Minerals in the E horizon are Hornblende (2.5%, mostly weathered), Plagioclase (2.6%, mostly weathered), Alkali-feldspar (18.1%, partly weathered), and Muscovite (0.6%). Biotite was no longer present.

The Sva 3 peat site is located in a flat area of *Sphagnum*, 20 m from the stream. The dark organic layer is 60 cm thick. Below 60 cm depth, the mineral particle content increases, the reduced mineral horizon is dark grey, sandy and is derived from fluvioglacial sediments. The free ground water table dropped down to 50 cm depth during the very dry summer of 1997, and approached the soil surface during the summer 1998, which was a rather wet summer.

Sampling

Studies were conducted in the summers of 1997 and 1998. In 1997, a spruce-pine pair was studied both on the podzol (Sva 1-A) and the peat site (Sva 3-A). Each pair of spruce and pine stood no more than 2–3 m from one another, and had about the same diameter and height. One soil pit (surface area: 50 × 50 cm) was dug next to each tree, one meter from the base of their trunk. From each profile, soils were sampled per horizon, sieved at 4 mm and sealed in plastic bags. Soils were centrifuged in the lab (14000 t/min), resulting soil solutions were collected and immediately sealed to avoid evaporation. Groundwaters were collected from the peat. Each tree was cored at 30 cm above soil level and the cores were immediately sealed. Twigs and needles were also sampled from each tree.

In 1998, two additional spruce-pine pairs were chosen both on the podzol (Sva 1-B and C) and the peat (Sva 3-B and C). On the podzol, four soil pits were dug around each tree of the three pairs (A – also sampled in 1997, B and C) that were studied (24 soil pits in total), at a distance of one meter from the tree trunk. Soils were sampled per horizon from each pit and sieved at 4 mm. Roots were separated and collected. Roots of each horizon were gathered per tree. Groundwaters were collected at the bottom of each soil pit and also gathered per tree. Soil samples were bulked per horizon in order to obtain a mean soil profile for the podzol site. At the peat site, three pits were dug around each tree of the two pairs (B and C) studied in 1998 (12 pits in total), at one meter from the base of the trunks. Fine roots were collected in the white layer constituted by dead, but not yet decomposed Sphagnum. Living roots were not observed deeper than this layer. From each pit, bulk soils were sampled at different depths and soil solutions were collected in the field by manual pressure (because of their high water content), except for the deeper mineral horizon for which we used centrifugation. Solutions of each horizon (L+F, 0–20; 20–50 and 50–80 cm) were bulked in the field per tree. In order to obtain a mean peat profile, all soil samples were bulked per horizon. In summers 1997 and 1998, stream water samples were collected close to the peat site.

At both sites, all studied tree trunks were cored several times, at 30 cm height, following different directions, and their sap wood were collected. Tree ages, diameters (at breast height, "DBH") and height (using a Digital hypsometer Forestor vertex) were measured.

Samples preparation and analytical methods

The natural abundance of ^{18}O in xylem sap and soil water was measured, after equilibration with CO_2 (Epstein and Mayeda 1953) using a Finnigan Delta E spectrometer. The analytical accuracy was 0.1 δ ‰ (Mathieu and Bariac 1996).

Roots were grouped by tree species, first in the field, and then more precisely in the lab. Roots with a diameter less than 2 mm were selected, cleaned from soil particles in ultrapure water, and then finally using a paintbrush. All fine roots and sap wood samples were dried at 65 °C, and finely ground. A digestion bloc system (Tecator 40 1016) was used for digesting 0.5 g of sample in 10 ml of HNO_3 that had been purified by double distillation. Soils were air dried, then sieved at 2 mm. Exchangeable Ca and Sr were extracted by shaking twice 10 g of soil in 50 ml of high purity, one molar NH_4Cl, during one hour on both occasions. Aliquots of the fine earth of each mineral horizon were ground to uniform fine consistency in an agate mortar. Soils (100 mg) were digested overnight with 1 ml of HNO_3 (purified by double distillation) and 1 ml of high purity HF. After evaporation, the total bulk soil digestion was obtained by adding $HClO_4$ and H_2O_2, to suppress Ca fluoride formation and organic matter residues. All water samples were filtered (0.45 μ). Peat solutions were first centrifuged (20 minutes at 3500 t/min) prior to filtration.

All Ca and Sr concentrations were measured by ICP-AES except total Sr contents of soils measured by ICP-MS. For isotopic measurements, aliquots of samples containing about 500 ng of Sr were evaporated, treated with high purity HNO_3 + H_2O_2 in order to remove organic matter remains, then evaporated to dryness in Teflon beakers. Samples were dissolved with 2 molar HCl and passed through ion exchange columns containing 8 ml of a Temex 50WX8, 200–400 mesh resin. Sr was collected after elution by HCl 2N and 4N and evaporated to dryness. The concentration of Sr in chemical blanks was lower than 2 ng L^{-1}. The $^{87}Sr/^{86}Sr$ isotopic

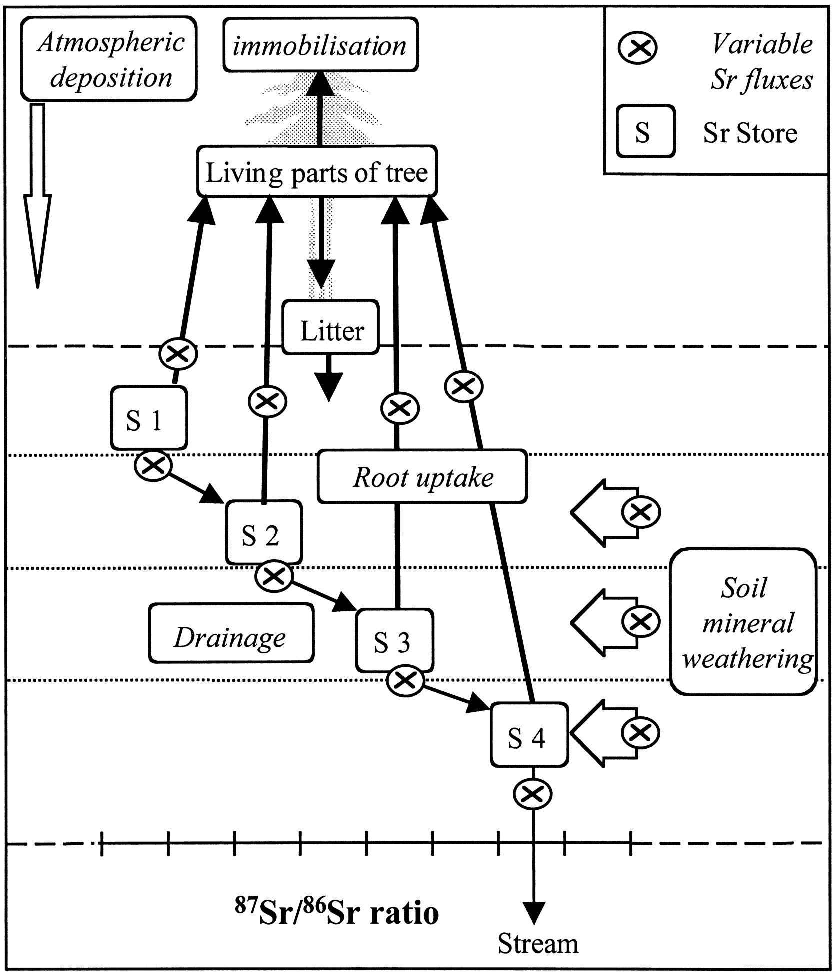

Figure 1. Representation of modelled Sr fluxes, stores and corresponding $^{87}Sr/^{86}Sr$ isotopic ratios.

Table 1. Annual fluxes of Ca (kg ha^{-1} yr^{-1}) and Sr (g ha^{-1} yr^{-1}) in the Svartberget catchment, used as input parameters in the model.

Deposition	1.4	
Runoff	37	
	Spruce	Pine
Litterfall	35.4	3.8
Immobilisation	24.4	11.8
Sr supplied by soil (Runoff + Immob − Dep.)	60	47.4

ratio of considered three periods: (1) an initial period where the vegetation was a heathland, dominated by *Vaccinium* and *Erica*, (2) an intermediate, twenty year period which corresponds to the establishment of the trees, and during which heathland parameters are progressively replaced by the new forest parameters and (3) the present period, where the vegetation is an adult spruce or pine stand. At the end of the initial period, we supposed that the ecosystem was in equilibrium, which allowed us to calculate all initial Sr stores and isotopic ratios in soils.

Some parameters were measured or taken from the literature (Table 1). Sr fluxes in atmospheric deposition and runoff from the catchment were computed from water monitoring (Grip and Bishop (1990) and Hornung et al. (1990); K. Bishop unpublished) and monthly analysis of rain and streamwater. The $^{87}Sr/^{86}Sr$ ratio of local rain (0.7164) was taken from Wickman (1996). Sr and Ca accumulation in pine and spruce wood as well as cycling in litterfall were calculated from local information on stand density and growth (Albrektson and Lundmark 1991), literature data on litterfall (Albrektson 1988) and the concentrations measured in our study. The forest vegetation was treated as mono-specific stands of pine or spruce, with an annual litterfall of 1000 kg ha^{-1} for both species and sites. The annual trunk wood increment was 2250 kg ha^{-1} yr^{-1} at the podzol site, and 1350 kg ha^{-1} yr^{-1} at the peat site. The Sr immobilisation in health vegetation was neglected (Brinkmark 1977). Drainage of Sr from the catchment was computed from measured output fluxes. The amount of Sr released from the soil by weathering was computed by mass balance, assuming that the sum of the Sr inputs coming from atmospheric deposition and released by mineral weathering should be close to the sum of the outputs in the form biomass immobilisation and drainage to runoff. This assumption is based on the fact that acidic deposition is extremely low at that site (Ilvesniemi et al. 2000).

We established an automatic procedure to calculate the unknown parameters. Starting from an initial set of parameters, the program modifies those parameters randomly and accepts or refuses this modification depending on whether it reduces or increases a fitting function. This fitting function is a weighted average of the differences between the observed and calculated values of isotopic ratios and Sr stores. Furthermore, if a set of parameters makes a soil horizon empty before 100 years, the fitting function returns a very high value.

For every set of measures, we repeated the automatic procedure several times, which delivered a set of possible solutions.

Results

Variations of Sr and Ca concentrations

At both sites, Sr and Ca (Table 2) concentrations in trunk wood, twigs and needles were always higher in spruce than in pine. In spruce, Sr concentrations strongly increased from trunk wood to twig but increased only slightly from twig to needle. In pine, Sr concentrations increased slightly from trunk wood to twig but decreased

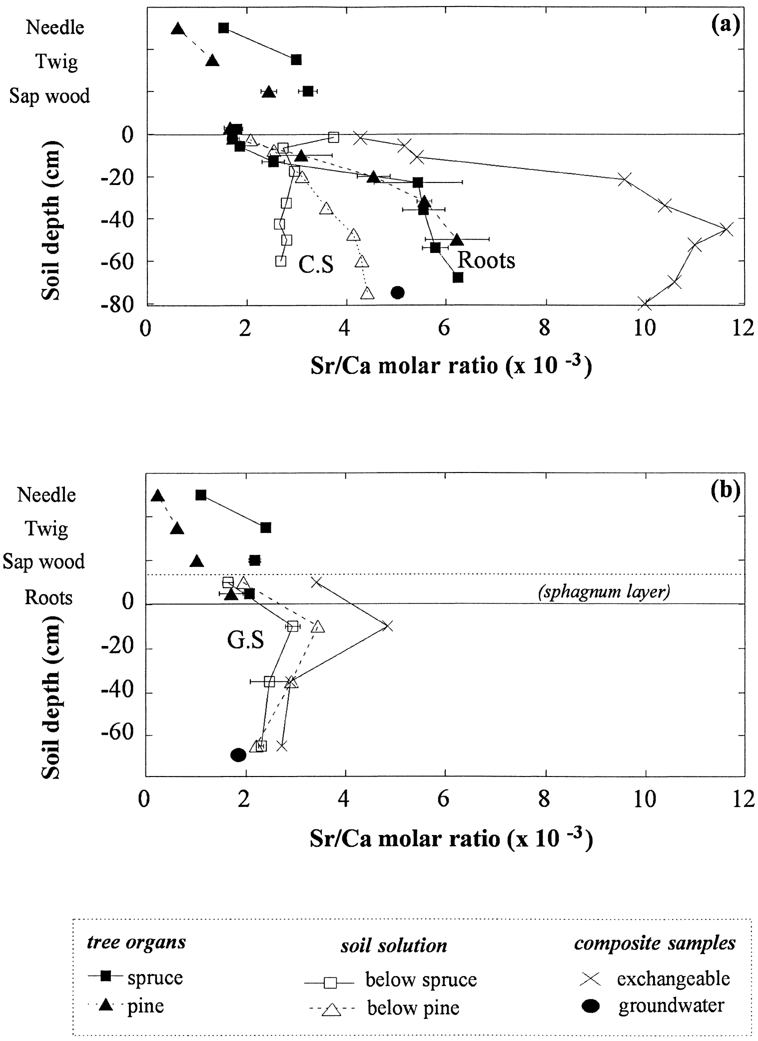

Figure 2. Variation of Sr/Ca ratios at the podzol and peat sites. (a) Sva 1, podzol: Sr/Ca molar ratio in spruce and pine organs (mean ± standard error (se) of couples A, B, C), in soil capillary solutions (C.S) below spruce and pine (couple A), in a composite sample of groundwater below couples A, B, C, and on the soil exchange complex from composite samples below couples A, B and C. (b) Sva 3, peat. Sr/Ca molar ratio in spruce and pine organs (mean ± standard error (se) of couples A, B, C), in soil solutions below spruce and pine (mean ± se of couples B and C), in a composite sample of groundwater below couple A, and on the soil exchange complex from composite samples below couples B and C.

from twig to needle. The trend was generally in the same direction as for Ca, but the Sr/Ca molar ratio (Figure 2) decreased from trunk to needle.

At the podzol site, root Sr concentrations and Sr/Ca ratios were similar in pine and spruce, and regularly increased with depth (Table 2). Exchangeable Sr (Fig-

Table 2. Sr concentrations in spruce and pine organs at the podzol and the peat sites.

Organ	Podzol		Peat	
	Spruce	Pine	Spruce	Pine
Needles	35.4	3.8	23.5	1.5
Twigs	25.7	7.5	22.0	3.6
Sapwood	5.4	2.6	3.9	1.2
Near surface roots (0–10 cm)	10.7	8.2	12.7	8.3
Deep roots (BC horizon)	49.3	59.8	absent	absent

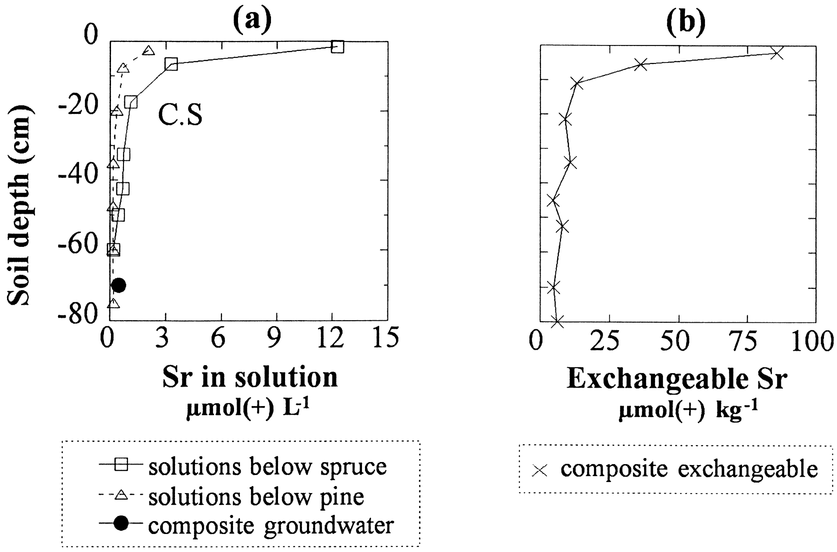

Figure 3. Sva 1, podzol. Sr concentrations (a) in soil solutions below spruce and pine, and in groundwater; (b) on the soil exchange complex. Symbols as in Figure 2.

ure 3) and Ca concentrations rapidly decreased from high levels in the humus to very low levels in the mineral horizons. Nevertheless, Sr (and Ca) concentrations in the soil solution of upper horizons were higher below spruce than below pine (Figure 3a). From H/ E horizons to Bh/ Bs horizons, the Sr/Ca molar ratio increased in roots and especially on the exchange complex (Figure 2a), but not in soil solutions. Bulk soil Sr and Ca contents (Table 3) were slightly lower in the E horizon and higher in the BC and C horizons. In comparison to the podzol site, exchangeable Sr (Figure 4) and Ca concentrations were high at the peat site. Concentrations and Sr/Ca ratios in solution and on the exchange complex varied little in the organic layers (Figure 2b and Figure 4). Concentrations in soil solution extracted by centrifugation from the deeper, mostly mineral layer, were higher than in groundwater, and stream water.

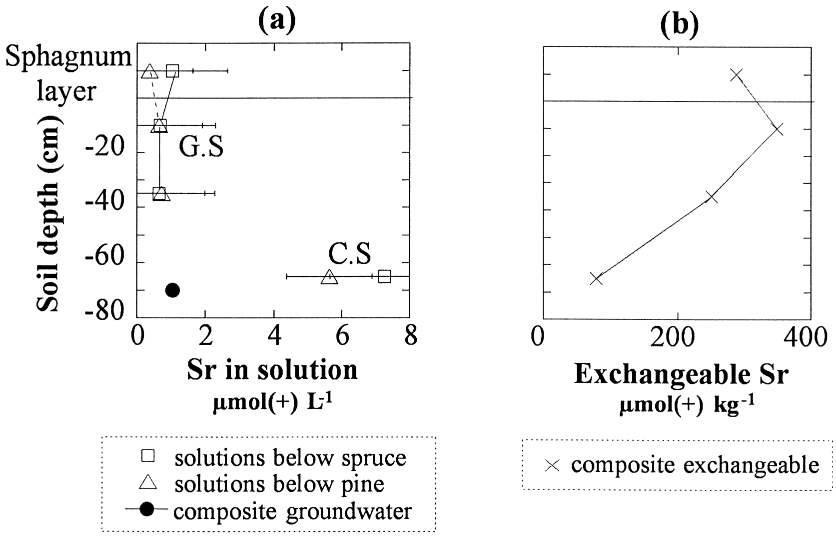

Figure 4. Sva 3, peat. Sr concentrations (a) in soil solutions extracted by manual pressure (G.S) or centrifuge (C.S) below spruce and pine, and groundwater; (b) on the soil exchange complex. Symbols as in Figure 2.

Table 3. Bulk soil total C, Ca, Mg, Na, K, Fe, Sr concentrations and $^{87}Sr/^{86}Sr$ ratio in the podzol profile and in the peat's deep mineral horizon.

Horizon depth	pH	C	Ca	Mg	Na	K	Fe	Sr	$^{87}Sr/^{86}Sr$
cm	water	g kg^{-1}					mg kg^{-1}		
Sva 1: Podzol									
A (4–7)	4.1	127	11.1	2.7	8.6	12.0	4.4	172	0.74001
E (7–15)	4.2	17	10.1	3.3	8.1	12.6	5.4	158	0.74445
Bh (19–24)	5	16	11.2	5.5	8.9	12.2	15.6	172	0.74486
Bs (24–44)	5.5	10	11.1	4.6	9.7	12.9	13.3	183	0.74523
BC (44-7)	5.5	nd	12.5	5.0	10.5	12.4	11.3	193	0.74294
C (> 70)	5.6	nd	13.0	5.3	10.5	12.7	10.7	197	0.74158
Sva 3: Peat									
H3 (50–80)	3.6	72	11.0	2.9	10.8	13.1	5.1	193	0.74291

In the deep mineral horizon of the peat (Table 3), bulk soil Ca, Mg and Fe contents were close to that measured in the podzol surface horizon, while Sr, Na and K content were close to that measured in the BC and C horizons.

Isotopic variations at the podzol site

The variation of the $^{87}Sr/^{86}Sr$ ratio in wood and roots in relation to depth is presented for the three spruce-pine pairs at the podzol site in the (Figure 5). Wood $^{87}Sr/^{86}Sr$ ratio varied between 0.731 and 0.736, with the spruce having either a higher $^{87}Sr/^{86}Sr$ ratio (Sva 1-A and C) or a ratio close to that of pine (Sva 1-B). The evolution of root isotopic composition according to depth varied for each tree. Nevertheless, for each pair down to the Bh horizon, the isotopic ratio of spruce fine roots was systematically higher than that of pine. The root isotopic ratio generally increased with depth, but high isotopic values were obtained in the A and E horizons below the spruce trees of pairs B and C. The $^{87}Sr/^{86}Sr$ ratio of average soil exchangeable Sr (Figure 6) increased regularly in relation to soil depth, with the exception of high values in the A horizon. At each depth, the isotopic ratio of soil exchangeable Sr was close to the average $^{87}Sr/^{86}Sr$ of spruce and pine roots (Figure 6) and lower than bulk soil $^{87}Sr/^{86}Sr$ isotopic ratio. The bulk soil isotopic ratio strongly increased from the A to the E horizon and decreased from the Bs to the C horizon.

The $\delta^{18}O$ of the average soil water decreased with increasing soil depth. Spruce xylem sap $\delta^{18}O$ was higher than pine xylem sap $\delta^{18}O$ (Figure 7). These patterns were similar to previous summer observations by Bishop and Dambrine (1995).

Isotopic variations at the peat site

The variation of the $^{87}Sr/^{86}Sr$ ratio in wood and roots in relation to depth is presented for the spruce-pine pairs A and B+C (Figure 8). Wood $^{87}Sr/^{86}Sr$ ratio varied between 0.731 and 0.739, and the $^{87}Sr/^{86}Sr$ ratio of the spruce in each pair was higher than that of the corresponding pine. Soil solutions in 1997 (pair A) and in 1998 (pairs B+C) were always more radiogenic below spruce than below pine. In all profiles, the $^{87}Sr/^{86}Sr$ ratio of soil solutions and soil exchangeable Sr (Figure 8) increased with depth. In 1997 and 1998, the $^{87}Sr/^{86}Sr$ ratio of upper soil solutions was close to that of stream water while that of the deepest soil solutions was close to that of the bulk soil. At each depth, soil solutions were in isotopic equilibrium with exchangeable Sr (Figure 8b).

The $\delta^{18}O$ of peat water decreased from −11.5 ‰ just below the living *Sphagnum* to −13.2 ‰ at a depth of 10 cm (Figure 9). That value corresponded to the $\delta^{18}O$ value of groundwater and stream water. The xylem sap $\delta^{18}O$ of spruce (−12.4 ‰) and pine (−12.2 ‰) from pair A were higher than in groundwater.

Parameters adjusted by the model

In this paper, simulated Sr isotopic variations at the podzol site will only be presented. Comparable runs were effected with the peat data set and will be used in the discussion section. The simulation of the isotopic signature was satisfactory for spruce, but below pine the simulated value of the H horizon was always lower than the measured value. This discrepancy could be explained by two effects: (1) a seasonal variability leading to higher isotopic signatures during summer and early autumn (the period of our sampling) and (2) the influence of neighbouring spruce litterfall with a higher Sr isotopic ratio on the exchangeable Sr store signature below pine. The first effect was taken into account by modelling monthly Sr fluxes and isotopic variations instead of yearly ones but the fit was not significantly improved.

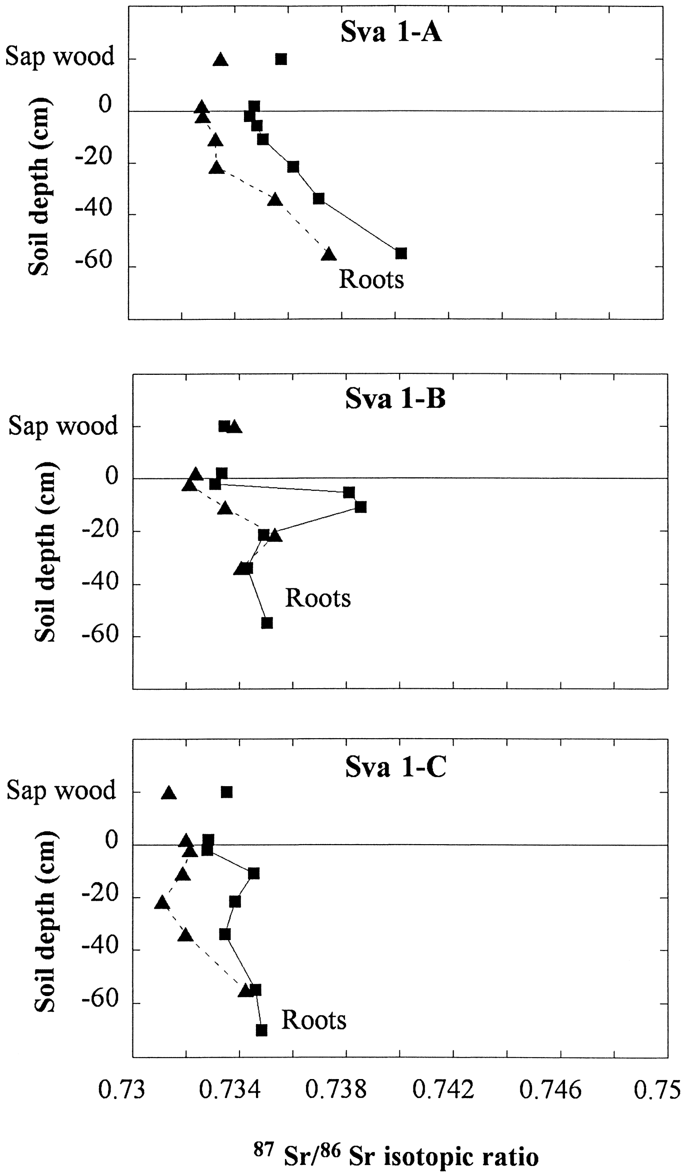

Figure 5. Sva 1, podzol. $^{87}Sr/^{86}Sr$ isotopic ratio in spruce and pine sap wood and roots in relation to depth of couples A, B and C.

The second effect was taken into account by considering a mixed stand, either dominated by spruces with 30% pine litterfall, or dominated by pines with 30% spruce litterfall. The resulting simulation was successful.

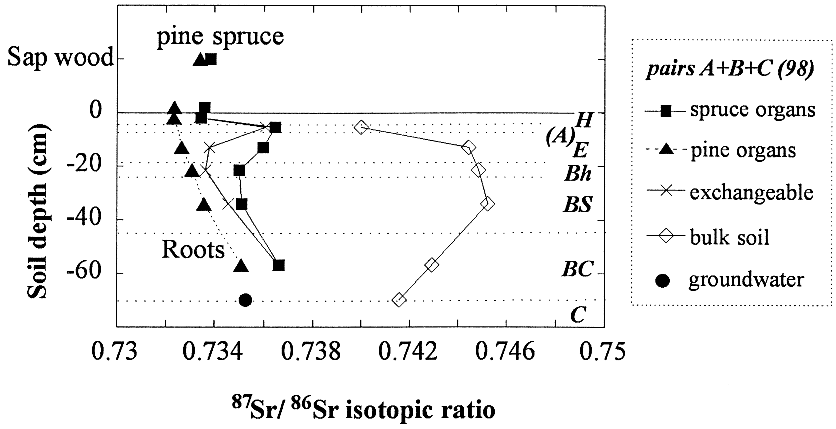

Figure 6. Sva 1, podzol. $^{87}Sr/^{86}Sr$ isotopic ratio of Sr in spruce and pine sap wood and roots (composite samples of couples A, B, C); exchangeable Sr and total Sr in the bulk soil; and soluble Sr in groundwater (composite samples below couples A, B, C).

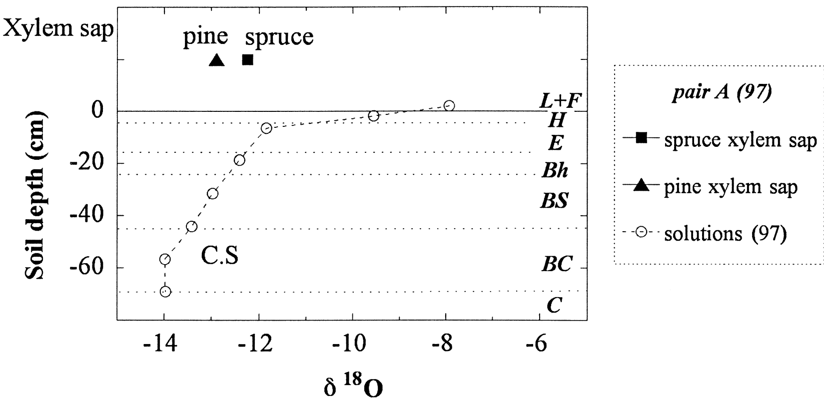

Figure 7. Sva 1-A, podzol. $\delta^{18}O$ in spruce and pine (couple A) xylem sap and in composite centrifuged waters collected under the two trees.

The parameters used for this simulation and the Sr isotopic ratios of trees and soils calculated by the model are illustrated in Figure 10.

Several parameters were adjusted differently by the model for the spruce (Figure 10a) and the pine (Figure 10b): the Sr isotopic signature of weathering in the E layer and the Sr flux released by weathering in all horizons were higher below spruce than below pine. The proportion of Sr uptake by spruce roots in the superficial layers was higher than that by pine roots.

Comparable results were obtained using parameters adjusted for the simulation of each spruce-pine pair (A, B and C) on the podzol and the peat site (data not shown).

In order to quantify the specific effect of spruce and pine on Sr cycling, we used the parameters of the pine ecosystem (Figure 10b) but replaced the deposition of Sr

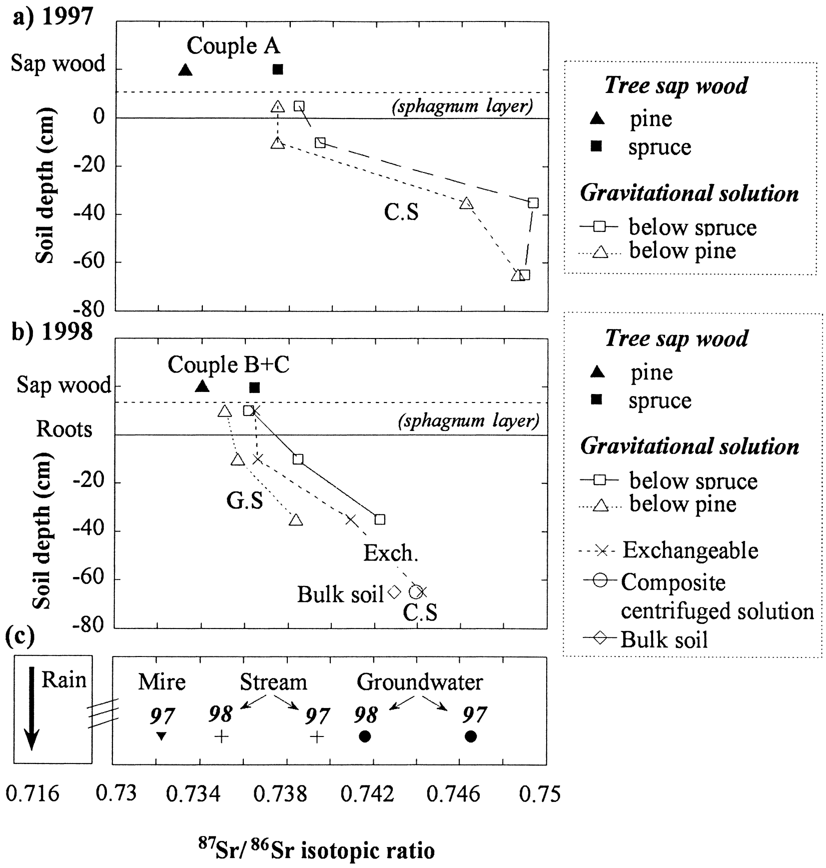

Figure 8. Sva 3, peat. $^{87}Sr/^{86}Sr$ isotopic ratio of Sr in spruce and pine sap wood and in centrifuged soil solutions below couple A in 1997, in spruce and pine organs (couples B and C), and in composite soil solutions samples below spruce and pine of couples B and C. Variations of $^{87}Sr/^{86}Sr$ isotopic ratio in stream and groundwater between 1997 (dry year) and 1998 (wet year).

in 100% pine litterfall (3.8 g ha^{-1}) by that of 100% spruce litterfall (35.4 g ha^{-1}). After 100 years, the model predicted that a pure spruce ecosystem would show a much higher $^{87}Sr/^{86}Sr$ ratio in needles (difference > 0.002) and in topsoil (difference > 0.005) than a pure pine ecosystem would. The difference was restricted to the upper soil horizon.

Discussion

Parameter calibration quality

The similarity between the results of the simulation and the measurements made in the field showed that our simple model was able to simulate the Sr biogeochemical

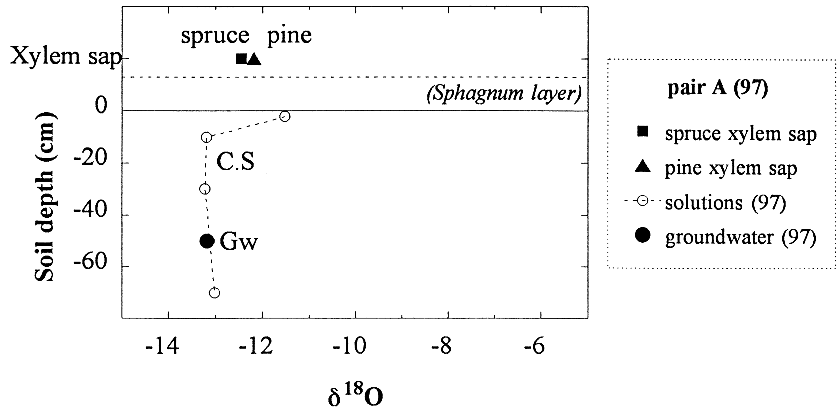

Figure 9. Sva 3-A, peat. $\delta^{18}O$ in spruce and pine (couple A) xylem sap and in composite centrifuged waters collected under the 2 trees.

cycling in a mixed forest ecosystem. Some of these fluxes were always in the same range from one simulation to another. For example, the percentage of Sr uptake simulated in the H layer was always lower than the ratio of litterfall to total uptake for the two species, because a higher proportion of uptake in this horizon, which is not supplied by weathering, would rapidly empty the horizon. In a similar way, the Sr drainage coefficient from the H layer was necessarily low, in order to reproduce the high Sr store, resulting from the high exchange capacity of organic matter. A peak of the isotopic signature of exchangeable Sr in the A-E horizon could be simulated only with a peak of the weathering isotopic signature in that layer. Nevertheless, the model could simulate this peak in the A-E horizon below spruce by adjusting a low weathering flux with a very high signature or a higher weathering flux with a signature that was not as high. Measured data were not available to help constrain the variation of some adjusted parameters. Due to these uncertainties in the calibration, and because of the spatial variability, it was not possible to evaluate precisely the Sr fluxes. The release of Sr by weathering (21, 9 and 23 g ha^{-1} yr^{-1} respectively in the E, BhBs and BC layers below spruce) in the simulation depicted by Figure 10 was judged realistic when compared to the historical release rates of Ca in the E and Bs horizons (Olsson and Melkerud 2000). Nevertheless, these fluxes were computed assuming Sr stores were close to steady state, which might not be the case (Bullen, unpublished).

Ca and Sr cycling at the podzol and the peat sites

Spruce cycling of Ca in litterfall was 3.5 times higher in spruce than in pine, as already noted by Alriksson and Eriksson (1998) (Table 1). The Sr cycling in litterfall was 12 times higher in spruce. Our model shows that this huge difference in cycling intensity has dramatic effects on Sr stores and isotopic ratios in trees and the upper horizons of the soil. Indeed, the model predicted that pure ecosystems would show a larger difference in $^{87}Sr/^{86}Sr$ ratio than what was observed in our

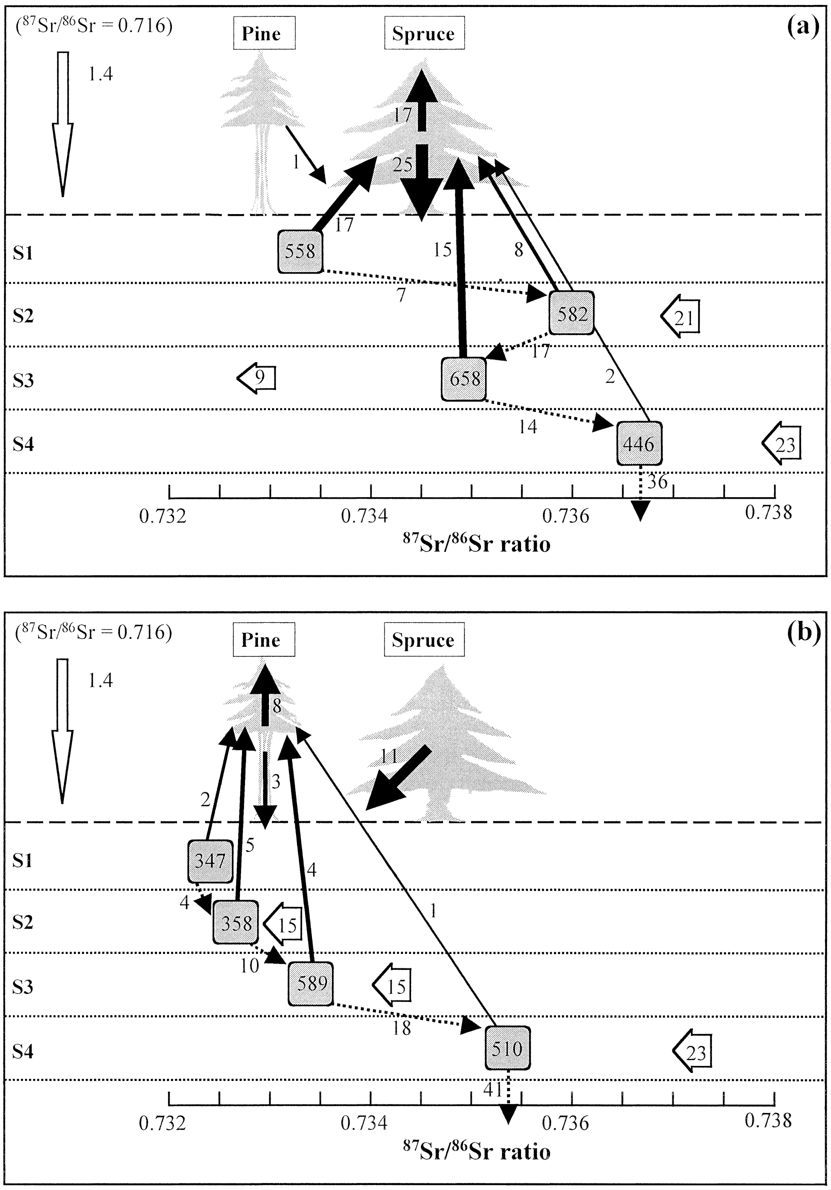

Figure 10. Predicted Sr stores (g ha^{-1}), fluxes (g ha^{-1} yr^{-1}) and $^{87}Sr/^{86}Sr$ ratio in (a) spruce with 30% pine litterfall and (b) pine with 30% spruce litterfall after 100 years of simulation, using adjusted parameters noted on the figure. The isotopic ratio of root available Sr in each soil horizon is given by the center of the square. The isotopic ratio of the Sr released by weathering is given by the extremity of the arrows.

spruce/pine comparisons, probably because of the mixing of the spruce and pine litter. This litter mixing, which was not measured, is rather logical as trees stood a few meters apart. However, because the difference in Ca cycling between species is less important than for Sr, the influence of tree species on Ca storage in the soil was not as high.

Origin of Sr in soils

Podzol

Although the $^{87}Sr/^{86}Sr$ ratio of individual minerals was not measured at that site, the variation of bulk soil $^{87}Sr/^{86}Sr$ ratio with depth was consistent with the variation of total soil contents and soil mineralogy as described by Olsson and Melkerud (2000). From the C horizon, up to the Bs horizon, decreasing bulk soil Ca and Sr concentrations as well as increasing bulk soil $^{87}Sr/^{86}Sr$ ratio and decreasing exchangeable Sr and $^{87}Sr/^{86}Sr$ ratios could be related to the weathering of Ca bearing minerals, such as hornblende. From the Bs up to the A horizon, the increase of exchangeable Sr isotopic ratio and decrease of bulk soil isotopic ratio was consistent with the loss of Mg and Fe corresponding to the intense dissolution of biotite. High root $^{87}Sr/^{86}Sr$ ratios (Figure 6) were measured only below two spruces (B and C, see Figure 5). This may be attributed to lateral variations of soil mineralogy. However, taking into account the high mineral requirements of spruce compared to pine, it suggests a species-specific weathering of minerals in the rhizosphere of this A horizon. At several podzol sites, including the Nyänget profile in the upper slope of this catchment, Jongmans et al. (1997) and Van Breemen et al. (2000) showed that mycorrhizal hyphae were able to penetrate and dissolve K feldspar present in the E horizon. The higher $^{87}Sr/^{86}Sr$ ratio in the A and E horizons below spruce could result from more aggressive spruce roots or mycorrhizal association exudates possibly related to the higher mineral requirements of spruce.

Nevertheless, A-E horizon provided variable amounts of Sr to spruce. In fact, a large contribution would have shifted the tree isotopic ratio towards that of roots in this horizon, which was not the case for spruce B (in Figure 5) for instance. This is surprising, if we consider that the rhizosphere of spruce had a positive effect on mineral weathering, but might be explained by the fact that Sr is not essential to the plant.

Peat

The Sr isotopic gradient in the peat was more regular than in the podzol, in relation to the organic nature of the peat and the supply of Sr from the fluvioglacial sediment via groundwater table fluctuations. The close $^{87}Sr/^{86}Sr$ ratios of mean soil solutions and exchangeable Sr indicate an apparent equilibrium between these two compartments in the peat profile. Compared to the podzol site, the higher $^{87}Sr/^{86}Sr$ ratio of available Sr in the peat, especially in the deep mineral horizon, may result from several processes. (1) Although of local origin, the mineralogy of the fluvioglacial deposit may differ from that of the till. (2) Biotite weathering is favoured in hydromorphic conditions. (3) The isotopic ratio of the Sr released by weathering from the till and the fluvioglacial deposit may be similar but the finer particle size of the fluvioglacial deposit may provide a larger Sr flux. As at the podzol site, the model showed that differences in Sr cycling could explain differences in topsoil $^{87}Sr/^{86}Sr$ ratios between species. But differences in deeper horizons were probably caused by unexpected lateral variations of the sediment composition.

Depth of water and Sr uptake.

In the podzol, soil solution $\delta^{18}O$ decreased with depth in accordance with the superposition of precipitation with isotopic signatures that vary seasonally (Ehleringer and Dawson 1992). The comparison between the isotopic values of wood and associated root and water profiles confirmed the deeper water uptake by pine measured at the same site by Bishop and Dambrine (1995) and were in agreement with the deeper rooting of pine. In the peat, the soil solution and groundwater $\delta^{18}O$ were homogeneous below 10 cm depth (Figure 10). The xylem sap $\delta^{18}O$ suggested that the water uptake of both pine and spruce was close to the surface even if, when measurements were effected, the water table was low.

Measuring or comparing the depth of Sr and Ca uptake by trees in a mixed stand appeared a more difficult task than was formerly thought, because of the potential effects of different Sr cycling intensities and specific mineral weathering discussed above. It should be done by comparing individual tree and soil isotopic composition. The use of average values for soils may lead to erroneous conclusions. Furthermore, Z shaped depth profiles of Sr isotopic ratio complicate the use of these data to establish uptake depths.

At the podzol site, the Sr absorption profiles calculated by our simulations showed the following patterns: (1) the main Sr sources for the spruces are the H and BHS horizons, the Sr taken up in A-E horizon being always lower; (2) the main Sr sources for the pines are often the A-E and BHS horizons, but sometimes also the H layer; (3) the average depth of Sr absorption is not significantly different between the two species (*ca* 20 cm). At the peat site, Sr was taken up by both species from the upper layer.

Cycles of Sr and Ca were not completely similar (Poszwa et al. 2000). For both species and sites, the decrease of the Sr/Ca ratio from roots to needles showed that Ca, compared to Sr, was preferentially mobilised within the tree, causing a relative accumulation of Ca in the foliage and litter. This decreased the Sr/Ca ratio of the topsoil. But the variation of Ca and Sr concentrations with depth followed the same pattern. It is likely that an average uptake depth calculated for Sr could be used for Ca.

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