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The concentration of Ca, Sr, Ba and Mn in successive needle age classes of Norway spruce [*Picea abies* (L.) Karst.]

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Abstract The concentrations of Ca, Sr, Ba and Mn were determined in up to five successive needle age classes from 54 individual Norway spruce trees [*Picea abies* (L.) Karst.] from nine different sites. The accumulation behaviour was found to be very nonuniform, going from an increase with needle age to a decrease; irregular patterns were also found. The type of accumulation is largely site specific. The increasing behaviour can in most cases be approximated by a simple arithmetic function. All four elements usually show the same accumulation pattern, the similarities being closest between Ca and Mn and least between Ca and Ba. It is postulated that the similarity between the four elements is due to their precipitation and storage as oxalates. The similarity between Ca, Sr and Ba is observed at all concentrations, that with Mn only at concentrations larger than 300 µg/g. Mn at small concentrations (< 50 µg/g) shows a decreasing pattern and no similarity at all with Ca, Sr and Ba, but behaves similar to mobile elements.

Key words Calcium · Barium · Manganese · Strontium · *Picea abies* needles

Introduction

It is well known that the concentrations of most elements in needles change with time (Fiedler et al. 1973; Nambiar and Five 1987; Cape et al. 1990). These changes are connected to the processes involved in the uptake, transportation, storage and retranslocation of the elements. Since concentrations in leaves are often considered to be an indicator of the nutritional status of a plant (Marschner 1986), much information is available on Ca and Mn (and other nutrients), whereas nonessential elements such as Sr and Ba have

received practically no attention. Moreover little effort has been made to link changes of concentrations in a quantitative way to the needle age class.

Those conifers that keep their needles for several years are especially suitable for the study of time related processes. Collecting needles of the different age classes at one specific date results in samples with a time spacing of one year, and the total time scale may span several years. With good approximation it can be supposed that the mean availability of the elements and the mean climatic factors did not change much over the few years involved. Collecting all samples at one date also eliminates the effects that the season exerts on the concentration of the elements (Adamowicz et al. 1993). The differences remaining between successive age classes therefore are connected mainly to their physiological age, i.e. to time.

The present work was undertaken to establish the changes that occur in successive needle age classes of Norway spruce trees growing in their natural environment. In contrast to most previous work, trees were sampled and the results treated individually. In order to determine if the changes with time depend on the actual concentrations involved, an attempt was made to cover as large a concentration range as possible by sampling trees at various sites over different bedrocks and soils. The entire work involved the investigation of 26 elements. Several distinct patterns of accumulation were observed, and the various elements showed grouping according to their accumulation behaviour (Wytttenbach et al. 1995). One such group consists of Ca, Sr, Ba and Mn, which proved to have a unique and closely related behaviour and which will be treated here in more detail.

Material and methods

Norway spruce was sampled by cutting branches from the upper third of the crown in November. The trees were 30–200 years old. Twigs were sectioned from the branches according to the age of their needles, and age classes 1 to 5 were usually collected. Adhering dust and aerosols were removed by washing with tetrahydrofuran/toluene

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Table 1 Site and sampling information

Site	Locality and country	Bedrock	Soil	pH (CaCl ₂) rooting zone	Sampling year	Number of trees	Needle age classes	
ALP	Alpthal, SZ	CH	flysch	humic gleysol	3.6–4.8	1990	5	1–4
AUE	Auenstein, AG	CH	limestone, partially covered by moraine	gleyic cambisol	3.5–3.9	1992	8	1–5
CHA	Chanéaz, VD	CH	moraine	gleyic luvisol	3.3–3.8	1992	8	1–5
GRO	Grossalp, GR	CH	moraine over limestone	eutric cambisol	4.6–6.7	1990	5	1–4
REG	Regelsberg, SG	CH	freshwater molasse	gleyic cambisol	7.6–7.7	1991	8	1–5
SAR	Sardona, SG	CH	flysch (quartzite)	orthic podzol	3.2–3.5	1990	5	1–4
SCH	Schluchsee, Black Forest	D	granite	orthic podzol	3.3–3.8	1989	9	1–3
SKO	Skogaby, Halmstad	S	gneiss	haplic podzol	3.1–3.9 ^a	1993	5 ^b	1–5
VIL	Villingen, Black Forest	D	red beds (sandstone)	dystric cambisol	3.2–3.9	1991	6	1–5

^a original data pH(H₂O) 3.9–4.5

^b combined into a composite sample

(Wytenbach et al. 1992). The twigs were dried, the needles separated from the twig axis and ground.

Samples were collected from nine sites over different bedrocks, sampling from five to nine trees per site (Table 1). Trees were sampled and analysed individually, except at site SKO, where five trees were combined into mixed samples. A total of 237 samples from 54 individual trees and 5 mixed samples were processed. Each sample analysed contained only needles of one age class.

Analysis of Ca, Sr, Ba and Mn was done by inductively coupled plasma emission spectroscopy after digestion with HNO₃/HClO₄ or directly by instrumental neutron activation analysis of the needles (Wytenbach et al. 1992). With many samples both methods were used and found to differ by less than 5%. The experimental reproducibility of the determinations was better than 3%. The results for the reference material NIST-1571 (orchard leaves, National Bureau of Standards, Washington, D.C.), which was inserted as a control sample at frequent intervals, were in agreement with accepted values. All analytical results are reported with respect to needles dried at 85 °C. The needle weight was determined by weighing 100 dry needles.

Removing dust and aerosols prior to analysis was necessary because the same samples were also analyzed for other elements, such as Fe and Al. Removing these contaminations would not have been necessary for Ca, Sr, Ba and Mn, since the exogenous contribution with these elements is small (<2%) with respect to their

endogenous concentrations. Exceptions are needles with very low concentrations of Ba and Sr (~ 1 µg/g), where the exogenous contribution is about 20%.

The following abbreviations are used: AC is the needle age class; AC1 denotes needles sprouted in the current year, AC2 in the year before and so on. Ca1 is the Ca concentration in AC1. CV is the relative standard deviation or coefficient of variation. The term biodynamic curve is used to refer to the sequence of the concentrations as a function of the needle age class, with all samples taken at the same date.

The iterative approximation of the non-linear Eqs. 1 and 2 to the experimental data was done by the method of Gauss-Newton (SAS, 1989). Data for site means were fitted directly. If individual trees were fitted together, their values were first normalized (Wytenbach et al. 1995).

Results

Concentrations

A summary of the range of concentrations found with AC1 is given in Table 2, where the ratio $F = \text{MAX}/\text{MIN}$ is used

Table 2 Range of concentrations (needle age class 1)

	Entire data set (54 trees, 9 sites)						Single sites (average values)	
	Individual trees			Site means ^c			Individual trees	
	MIN ^a	MAX ^a	F ^b	MIN	MAX	F	F	CV ^d
Ca	1477	7241	5	2170	6600	3	1.7	22
Sr	0.4	41	100	1.1	36	33	2.6	29
Ba	0.3	70	221	1.0	52	52	3.3	39
Mn	9	3082	354	33	2537	77	2.2 ^e	30 ^e

^a MIN and MAX are the lowest and the highest concentration (µg/g)

^b F is the ratio MAX/MIN

^c Arithmetic means, except MIN for Mn (geometric mean)

^d Average relative standard deviation (%) or intersite variation; n per site as in Table 1

^e Excluding site REG, where Mn has a very large distribution (F = 10 and geometric standard deviation 2.7)

Table 3 Site means of the concentrations (µg/g) in age class 1 and type of biodynamic curve for Ca of the individual trees. Sites are ordered according to the Ca value; n per site as in Table 1. Means are arithmetic, except for Mn at REG (geometric mean)

Site	Ca	Sr	Ba	Mn	Type of curves (Ca) ^a
VIL	2170	3.2	15.8	1286	B(5), A(1)
SKO	2449	6.6	6.9	1736	C(5)
SCH	2740	1.1	1.0	493	C(4), D(4), A(1)
SAR	3707	8.8	13.3	602	B(3), A(1), C(1)
REG	4067	29.8	30.8	33	A(8)
AUE	4070	5.6	21.2	1980	A(8)
ALP	4303	36.0	29.6	193	A(7)
CHA	5265	17.3	51.8	2537	A(8)
GRO	6600	18.3	21.3	197	A(5)

^a Letters refer to the form of the curves shown in Fig. 1: A asymptotic increase, B irregular, C approximately constant, D decreasing. Values in brackets give the number of trees

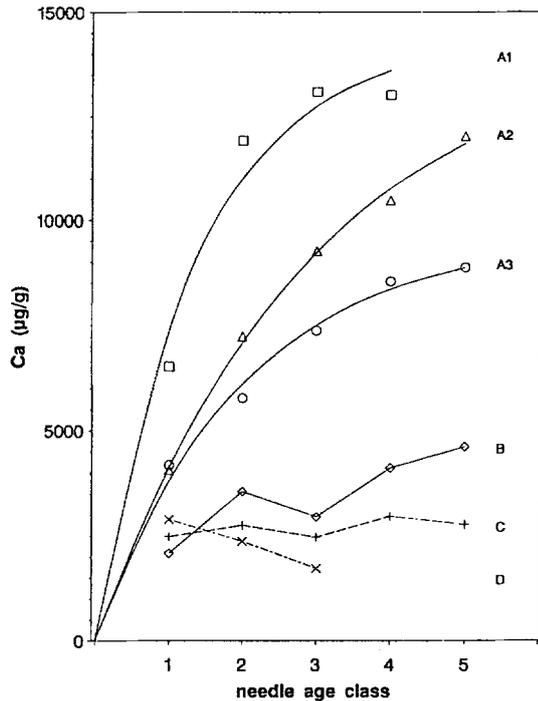


Fig. 1 Various types of the biodynamic behaviour of Ca. The values refer to means of those trees from one site that behave identically: A1 GRO (all 5 trees), A2 REG (all 8 trees), A3 AUE (all 8 trees), B VIL (5 out of 6 trees), C SKO (mixed sample from 5 trees), D SCH (4 out of 9 trees). The curves A1, A2 and A3 are the functions given by Eq. 1 with the parameters from Table 6

as a measure of the range. The various site means are listed in Table 3. Considering the whole population investigated, F is moderate for Ca and much larger for the other elements, increasing as $\text{Ca} \ll \text{Sr} < \text{Ba} < \text{Mn}$; this holds as well for individual trees as for site means. Considering single sites, the average variation between trees (i.e. the mean intrasite variation) increases with $\text{Ca} < \text{Sr} < \text{Ba}$. The variation of Mn is similar to that of Sr at all sites except REG, where Mn has an extremely wide distribution.

Table 4 Variation of Ca, Sr, Ba and Mn with the needle age class at site AUE (mean of eight trees). All four elements increase smoothly according to Eq. 1

AC	Ca µg/g	Ca µg/needle	Sr/Ca 10^{-5}	Ba/Ca 10^{-5}	Mn/Ca 10^{-3}
1	4070	10.8	139	522	490
2	5814	18.0	134	482	473
3	7475	25.3	126	433	473
4	8579	30.7	120	402	493
5	8866	32.3	118	400	501

Table 5 Variation of Ca, Sr, Ba and Mn with the needle age class at site VIL (mean of 5 out of 6 trees). All four elements increase irregularly

AC	Ca µg/g	Ca µg/needle	Sr/Ca 10^{-5}	Ba/Ca 10^{-5}	Mn/Ca 10^{-3}
1	2089	14.2	136	700	651
2	3563	25.2	125	594	544
3	2959	20.7	131	592	549
4	4133	31.9	129	586	513
5	4628	33.2	128	580	514

Biodynamics of Ca

The biodynamic behaviour of Ca shows great diversity, going from an increase with time to a decrease. Individual trees at a given site do not always behave in the same way. Table 3 shows that most deviations from site-uniformity are found at sites with low Ca1 values, whereas at sites with high Ca1 values all trees behave almost identically. Typical examples for biodynamic curves (given as means of those trees from one site that behave in the same way) are shown in Fig. 1 and in Tables 4 and 5.

The sites AUE, CHA, GRO and REG show a strong and regular increase. At each of these sites, the individual trees closely follow the same pattern. The increase with time is not linear, but tends to level off at high ACs. This behaviour can be described by the function

$$c(t) = A(1 - e^{-\lambda t}) \quad (1)$$

Table 6 Results from fitting Eq. 1 to the experimental data

Data source	Type of samples	Number of data points	Ca			Sr			Ba			Mn		
			A (µg/g)	λ (year ⁻¹)	Fit ^g (%)	A (µg/g)	λ (year ⁻¹)	Fit (%)	A (µg/g)	λ (year ⁻¹)	Fit (%)	A (µg/g)	λ (year ⁻¹)	Fit (%)
REG this work	c	40	14643	0.33	6	61	0.70	5	45	1.04	6	does not apply		
AUE this work	c	40	9655	0.50	11	11	0.71	9	36	0.89	9	4632	0.47	12
GRO this work	d	20	14400	0.72	11	34	0.93	12	32	1.20	13	325	0.99	12
CHA this work	c	40	8693	0.86	7	21	1.80	8	does not apply			3933	0.91	7
Postturm ^a	e	5	6702	0.51	4	no data			no data			3122	0.52	5
Stormstown ^b	f	10	10224	0.57	5	no data			no data			no data		

^a Rademacher et al. 1992 (Table 5)

^b Adamowicz et al. 1993 (Table 2, Plantation I, sampling September 1988 and November 1988)

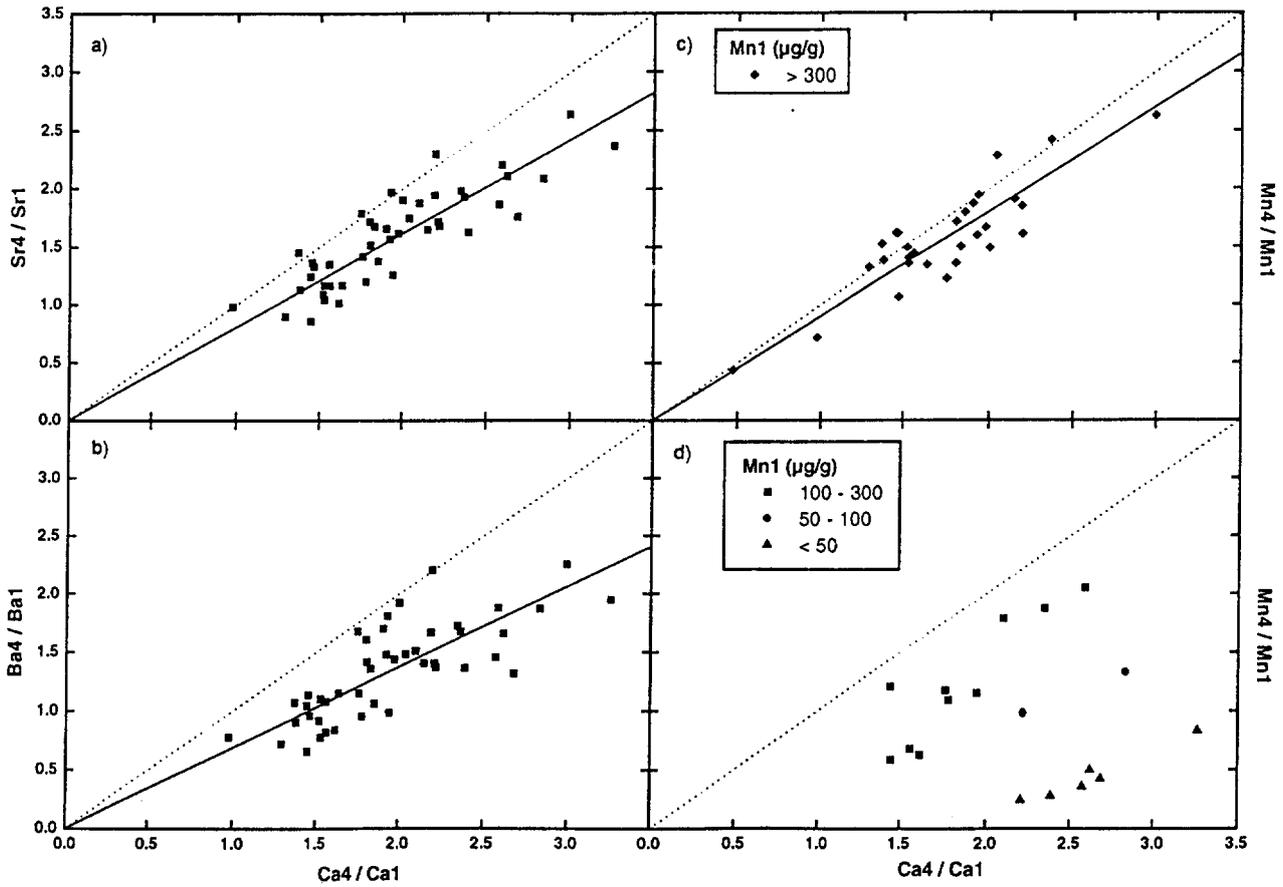
^c 8 individual trees, 5 AC

^d 5 individual trees, 4 AC

^e Mixed sample from 30 trees, 5 AC

^f Mixed sample from 22 trees, twice 5 AC

^g The fit is the scatter of the experimental data around the calculated values, expressed as the residual standard deviation. r^2 is > 0.986 in all cases



where $c(t)$ is the concentration in AC t ($t = 1, 2, \dots$) and A and λ are free parameters. The fitted functions are given by the curves A1, A2 and A3 in Fig. 1. Details of the fit of Eq. 1 are given in Table 6. The function describes the experimental data very well. The normalized data of the individual trees scatter around the calculated values (Fit in Table 6) at each site by about 9%. The parameters A and λ are site specific. The parameter A denotes the final concentration that is approached asymptotically, and λ is connected to the rate of this approach; a larger value of λ implies a faster approach to the final value than a smaller value of λ . As is indicated in Fig. 1, the function has the value zero at the hypothetical AC zero. The site ALP also shows a strong increase; however, the curve is not smooth in this case, and application of Eq. 1 does not seem justified.

Contrary to these sites, most trees at the sites VIL, SKO, SCH and SAR do not show a regular increase. Their curves are either irregularly increasing, more or less constant or even decreasing (curves B, C, D in Fig. 1). These sites have low Ca1 site means. With individual trees, however, the value of Ca1 is not an unequivocal indicator for the biodynamic behaviour, as may be seen from the fact that the two trees with the smallest and the highest Ca1 both have increasing concentrations. Nevertheless the following rules were found to apply with all trees: (a) if Ca1 > 4000 $\mu\text{g/g}$, the concentration rises with time, and (b) if Ca1 < 4000 $\mu\text{g/g}$, any form of biodynamic behaviour may be found.

Fig. 2 Scatter plots for the comparison of the relative changes between AC1 and AC4 of Sr (a), Ba (b) and Mn (c Mn1 > 300 $\mu\text{g/g}$; d Mn1 < 300 $\mu\text{g/g}$) with those of Ca. Dots represent individual trees. If AC4/AC1 is smaller than 1, the concentrations decrease, if it is larger, they increase when going from AC1 to AC4. Trees with equal changes in both elements fall on the dashed line (slope 1). The solid line is given by the regression analysis (results in Table 7)

Biodynamics of Sr

The main characteristic of the biodynamic behaviour of Sr is its similarity to that of Ca. This holds as well for trees where Ca increases regularly as for the other cases. The similarity between Sr and Ca is observed at all Sr concentrations.

At sites with regularly increasing values, the data can be fitted by Eq. 1; results are given in Table 6. The scatter around the calculated values is similar to Ca, but the values of λ are larger for Sr than for Ca at every site, pointing to small and systematic dynamic differences between Sr and Ca.

These small differences are also present in trees which cannot be fitted by Eq. 1. In Fig. 2a the ratio AC4/AC1, i.e. the relative change between AC1 and AC4, is used as a parameter that roughly describes the biodynamics of an element, irrespective of the actual form of the curve. In this diagram, an identical behaviour of Sr and Ca would produce points that fall on a line with slope 1, passing

Table 7 Statistical analysis of the comparison of the relative changes between AC1 and AC4 (correlation between y and x , see Fig. 2)

y	x	Figure	Trees	r^{2c}	Slope
Mn4/Mn1	Ca4/Ca1	2c	29 ^a	0.762	$0.90 \pm .02$
Sr4/Sr1	Ca4/Ca1	2a	45 ^b	0.733	$0.81 \pm .02$
Ba4/Ba1	Ca4/Ca1	2b	45 ^b	0.587	$0.69 \pm .02$
Ba4/Ba1	Sr4/Sr1	none	45 ^b	0.902	$0.85 \pm .01$

^a Only trees with Mn1 > 300 $\mu\text{g/g}$. Trees with smaller values of Mn1 are shown in Fig. 2d

^b All trees except SCH, where AC4 was not sampled

^c r^2 is the coefficient of determination. All correlations are highly significant ($P < 0.0001$), and all slopes are significantly smaller than 1.00

through the origin. This is found with only a few trees. All other points lie below this line. There is a strong positive correlation between Sr4/Sr1 and Ca4/Ca1 (Table 7). The slope of the regression line is 0.81. This indicates that the relative changes, when going from AC1 to AC4, are similar but generally somewhat smaller for Sr than for Ca.

Another way to document the small differences between Sr and Ca is to consider the ratio Sr/Ca as a function of the AC. Examples are given in Table 4 (site AUE, where both elements increase according to Eq. 1) and in Table 5 (site VII, where both elements behave irregularly). In these cases (as at all other sites) the ratio Sr/Ca decreases very slightly with time. The decrease is always smooth, i.e. it does not reflect any irregularities that may be present in the curves of the individual elements. Tables 4 and 5 refer to site means, but the same effects are also shown by the individual trees, although the numerical values of Sr/Ca are different for each tree.

Biodynamics of Ba

As with Sr, the biodynamics of Ba is similar to that of Ca in all trees, and this similarity is found at all Ba concentrations. At sites with regularly increasing values, the data can be described by Eq. 1; results are given in Table 6. The values of λ for Ba are larger than those of Sr and Ca at every site. Irrespective of the form of the curve, the differences to Ca are more pronounced with Ba than with Sr (Fig. 2b, Table 7); the scatter of the points is larger and the average slope (0.69) is smaller for Ba than for Sr.

The same effect may be seen from the ratio Ba/Ca as a function of the AC (Tables 4, 5). The ratio Ba/Ca decreases smoothly with time and does not reflect any irregularities that may be present in the curves of the individual elements. The changes of Ba/Ca with time, however, are about twice as large as those of Sr/Ca. With Ba, the differences to Ca are so large that with some trees Ba concentrations in older needles are actually decreasing, whereas Ca is still increasing or constant. This effect prevents fitting of the Ba values at CHA by Eq. 1.

The biodynamics of Ba is closer to that of Sr than of Ca. When Ba4/Ba1 is plotted against Sr4/Sr1 (not shown, values in Table 7), the resulting slope (0.85) is closer to

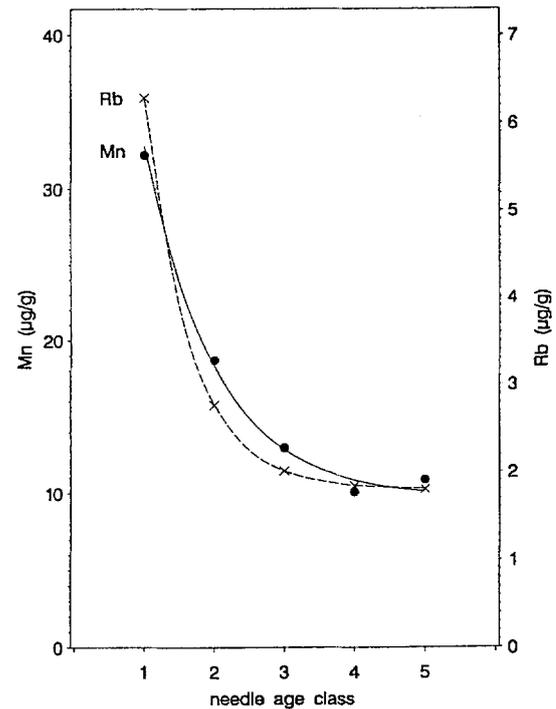


Fig. 3 Biodynamic behaviour of Mn (left scale) and of Rb (right scale) at REG. Points are experimental means (Mn: 6 trees with Mn1 < 50 $\mu\text{g/g}$; Rb: all 8 trees). Curves are given by Eq. 2 with the following parameters for Mn (and Rb): $A = 10$ (1.8) $\mu\text{g/g}$, $B = 23$ (4.5) $\mu\text{g/g}$, $\lambda = 0.99$ (1.53) year^{-1}

unity and the scatter of the points less than in Fig. 2b. Similarly the value of λ for Ba is closer to that of Sr than of Ca at all sites (Table 6).

Biodynamics of Mn

The dynamics of Mn clearly depends on the concentration. At low concentrations (Mn1 < 50 $\mu\text{g/g}$), the values decrease with time (Fig. 3). This decrease can be well described by

$$c(t) = A + B \cdot e^{-\lambda(t-1)} \quad (2)$$

In this concentration range there is no similarity at all between Mn and Ca. In fact, with the trees shown in Fig. 3, Ca increases according to Eq. 1 (see Fig. 1, curve A2), i.e. Mn and Ca change in the opposite direction. This uncoupling of the dynamics of Ca and Mn (at low concentrations) is also evident from Fig. 2d.

When Mn1 > 50 $\mu\text{g/g}$, the concentrations either decrease or increase with time or are irregular. In this concentration range, the dynamics of Mn begins to resemble that of Ca, becoming very similar to Ca in trees with Mn1 > 300 $\mu\text{g/g}$ as may be seen from the comparison of Fig. 2c and 2d. Nevertheless some small systematic differences between Mn and Ca persist. Although many trees fall close to the line with unity slope (indicating exactly equal dynamics), the mean slope (0.90) is somewhat smaller.

The same effect is also shown by the ratio Mn/Ca, which changes only little with time (Tables 4, 5). The changes in Mn/Ca are especially small after AC2. The mean CV of Mn/Ca between the different age classes (excluding AC1) is only 4% in the 29 trees with Mn1 > 300 µg/g, what is close to the analytical reproducibility.

At those sites where Mn > 300 µg/g and where Ca can be described by Eq. 1, this also holds for Mn (Table 6). At these sites (AUE, CHA, GRO) the parameter $\lambda(\text{Mn})$ is approximately equal to $\lambda(\text{Ca})$, indicating a very similar asymptotic increase of both elements.

Discussion

Concentrations

Table 2 shows that Ca has by far the smallest range of all four elements; this is probably connected to the role of Ca as an essential element. Sites with mean Ca1 < 3000 µg/g (VIL, SKO, SCH) have a bedrock of red beds, gneiss or granite, and the corresponding soils seem to be low in base cations and to entail relatively small Ca concentrations in needles. Sites over other types of bedrocks have considerably larger mean Ca1 values (Tables 1, 3). Literature does not give consistent values for the deficiency limit of Ca1 in Norway spruce. Accepting the value of 1000 µg/g (Hüttl and Wisniewski 1987), it may be concluded that all investigated trees have a sufficient Ca supply.

The concentrations of Sr and Ba are within the range of the few published data for conifers (Robarge et al. 1989; Santerre et al. 1990; Wyttenbach et al. 1985). Ba values are either roughly equal to or a few times larger than Sr values; this is often observed in plants and probably reflects the respective available soil concentrations. Sites with low Ca needle values also have low values for Sr and Ba, but high values for Al; the same tendencies are present in data given by Ke and Skelly (1994).

The deficiency value for Mn1 is given as 20 µg/g (Foy 1973; Hüttl and Wisniewski 1987). Two of the investigated trees have smaller values (9 and 16 µg/g), but do not show signs of chlorosis. All trees with Mn1 < 100 µg/g are from site REG with a bedrock of molasse and a soil pH of 7.6. On the other hand, the availability of Mn is very great on sites over moraines (AUE, CHA) with a soil pH between 3 and 4, where the highest value found was 3100 µg/g for Mn1 and 7600 µg/g for Mn5. This is consistent with the well known fact that Mn uptake is small from neutral or alkaline mineral soils and that Mn concentrations in plants are closely related to soil pH (Foy 1973; Wyttenbach et al. 1991b). Considering all trees, the range of Mn is very large (Table 2). In fact the range of Mn was found to be the second largest (after Cs) among all 24 elements determined in this work. A similar large range in Norway spruce (Mn1 from 2 to 3500 µg/g) has been reported by Kreutzer (1972) and Ke and Skelly (1994). Mn is therefore the one essential element with the largest range. Its concentration in many trees is much higher than the 30–500 µg/g that

are sometimes considered normal for plants (Clarkson and Hanson 1980). It almost reaches the values of Mn-accumulator plants such as *Acanthopanax sciadophylloides* and is well above values considered toxic for many species (Foy 1973). Norway spruce therefore seems to be very tolerant to Mn. Since there obviously is no reduced absorption or translocation to the needles, the tolerance is probably due to compartmentalization of Mn within the needles.

Biodynamic curves

One salient feature of the biodynamics of Ca (and also of Sr, Ba and Mn) is its diversity, both among the various sites (Fig. 1) and, to a lesser degree, among the individual trees on a given site (Table 3). This diversity is totally different from the uniform behaviour of many other elements in the same population. Si, Al, Sc, La, and the rare earth elements have been found to increase linearly in all trees and on all sites (Wyttenbach et al. 1991a, 1995), and similarly P, K, Rb and Cs always decrease regularly (Tobler et al. 1994).

Increasing concentrations for Ca and Mn are often reported in the literature for conifer needles and are sometimes considered to be the normal case (Cape et al. 1990). It should be noted that the increase is not linear with time, but asymptotic (Eq. 1 and curves A in Fig. 2). This asymptotic behaviour is also observed by other workers, and their data can usually be fitted well with Eq. 1. Two examples for Ca and one for Mn calculated from published data are given in the lower half of Table 6. In these cases the fit is even better than in the upper half of Table 6, which is due to the use of site means instead of the (not available) values from individual trees. The values of the parameters A and λ are similar to those found in the present work. In contrast to the ample evidence for asymptotically increasing values, evidence for irregular or decreasing biodynamics of Ca is scarce in literature. However, the few reported cases refer to sites on red beds (Anonymous 1986) or on gneiss and granite (Ferraz 1985), in agreement with the present findings.

Some investigators assume Ca uptake to be largely a passive mass flow regulated process. Transport to the leaves is known to be almost exclusively via the phloem, and retranslocation out of the leaves is considered to be extremely low or nil (Hill 1980; Marschner 1986). As the concentration present in the leaf at any time is the result of all previous influx and efflux, the above properties will lead to a linear increase of the concentration in the needles with time, if the mean annual concentration in the soil solution and the mean annual transpiration rate per gram of needles do not change over the 5 years that contribute to the information stored in AC1 to AC5. Such a linear increase was indeed found with all trees of the present population for Si and some other elements, but never with Ca, Sr, Ba and Mn. It is therefore obvious that the processes involved in the uptake, transport, storage and remobilization of the two groups of elements must differ fundamentally.

One possible explanation for the observed asymptotic curves could be a substantial loss of Ca, Ba, Sr and Mn (by retranslocation or other processes) out of the needle. A system with a constant input rate R and an efflux that is proportional to the accumulated content is described by $dCa/dt = R - \lambda \cdot Ca$. The integral form for this rate equation is indeed given by Eq. 1 with $A = R/\lambda$. However, the export rate found is unrealistically high ($\lambda = 0.3-0.9$ for Ca), meaning that about 50% of the accumulated Ca is exported again each year, and the export rate is even higher for Sr and Ba (Table 6). It is therefore doubtful if the mechanism described by the above differential equation is real. Another, more likely explanation for the asymptotic curves could be that Ca uptake in spruce is only partially proportional to the water uptake, i.e. the uptake rate R is not a constant as assumed above, but decreases with time to very small values because uptake is already controlled at the endodermal barrier and transport is largely by ion-exchange processes (Marschner 1986; Fink 1991).

Some of the observed irregularities in the curves are probably due to the fact that Ca uptake into AC1 may be very variable in different years. It has been observed by Evers (1972) that the same group of spruce, sampled in 8 successive years, showed differences in Ca1 reaching a factor of 2. If a year with very low uptake is followed by a year with very high uptake, this may be exhibited in the biodynamic curve as a negative difference between successive ACs and be mistaken to indicate remobilisation. The succession of 3 ACs with decreasing values (curve D in Fig. 1) may have a similar explanation. In the investigation by Evers, the inter-annual variation of Ca1 was much greater than that of the simultaneously measured P, K or N and was tentatively attributed to meteorological factors. However, since in the present work trees with irregular Ca curves also show a smooth and linear accumulation of Si and related elements, and since on a given site not all trees show Ca irregularities, the attribution to meteorological factors is not convincing. Evers made his investigation on a site over red beds, identical to VIL, where the biodynamics were found to be strongly irregular (curve B in Fig. 1). It is therefore probable that soil factors also contribute. On sites where the Ca concentration increases strongly with time, such irregularities are usually not found (Fig. 1, curves A), either because they are masked by the relatively strong uptake in later years or because uptake into AC1 does not change appreciably from year to year on these sites. It should finally be noted that the irregularities in the curves persist when the concentration is substituted by the content of a needle (Table 5); the irregularities therefore are not due to variations of the needle weight with the AC.

Comparison of Ca, Sr, Ba, and Mn

The second salient feature of the biodynamics is the similarity of Ca with Sr and Ba in all trees and with Mn in trees that have $Mn1 > 300 \mu\text{g/g}$. These similarities are always present, irrespective of the form of the Ca curve or of any irregularity in it. The deviations from behaviour

exactly equal to that of Ca are least with Mn, intermediate with Sr and most pronounced with Ba (Fig. 2). The ratios Sr/Ca and Ba/Ca decrease smoothly with the AC (Tables 4, 5). The ratio Mn/Ca decreases only between AC1 and AC2 and stays practically constant afterwards. While there are no published data for Sr and Ba, values for Ca and Mn usually also demonstrate this behaviour. Thus it can be shown from data for groups of Norway spruce that Mn/Ca is constant over all five ACs with a CV of only 1.8% (Rademacher et al. 1992, $Mn1 = 1214 \mu\text{g/g}$) or from AC2 to AC7 with a CV of 2.4% (Nilsson 1972, $Mn1 = 650 \mu\text{g/g}$). Kazda and Zvacek (1989), comparing the uptake of Ca and Mn into spruce needles during 2 seasons also noted "remarkably similar dynamics" of the two elements.

The similarity of the biodynamics of Ca, Sr and Ba and the position of Sr intermediate to Ca and Ba are in agreement with their chemical properties. All three elements are earth alkali metals and thus chemical homologues. Their ions have a valency of +2. They are class A ions with very similar ionic and covalent indexes (Woolhouse 1983). Mn is a transition metal, and Mn^{+2} is a borderline ion with an ionic index similar to Ca, but with a larger covalent index. Obviously these chemical similarities are responsible for the observed almost equal behaviour of all four elements during uptake and storage. A very important point is the chemical nature of the storage compound. Fink (1991) has shown by chemical speciation and by microscopy that Ca in spruce needles is mainly stored extracellularly as Ca-oxalate; the percentage of Ca present as oxalate goes from 60% at low total Ca concentrations to 90% at high concentrations. Ca is precipitated by the reaction with oxalic acid. In the same process any other ion forming an insoluble oxalate will also precipitate if its concentration is high enough to exceed its solubility product. The pertinent solubilities, given as mg metal-oxalate per L H_2O , are Ca 6.7, Sr 51, Ba 93, and Mn 312 (Bailar et al. 1973). Then a very crude estimate, based on a water content of the fresh needle of 50% and neglecting effects due to the actual oxalate concentration, to activity coefficients and to local effects within the cell (Robertson 1982), gives the following concentrations of the metals (expressed on a dry needle basis) that are equivalent to the above solubilities: Ca 2, Sr 20, Ba 60, and Mn $100 \mu\text{g/g}$. Comparing these values with the actual concentrations (Table 2) shows that the solubility of Ca is always exceeded and that of Mn at least in its upper concentration range. It is therefore highly probable that the simultaneous precipitation of Ca and Mn as oxalates is the reason for the observed constancy of the ratio Mn/Ca with the AC in every tree with $Mn1 > 300 \mu\text{g/g}$. The small deviations found in AC1 should be due to the fact that Ca is to some extent also present in other forms (water soluble compounds and Ca pectate; Fink 1991), where no close relation to Mn is expected, and that these forms contribute more to the total amounts in AC1 than in higher ACs.

The situation is more complex with Sr and Ba, where many trees have concentrations below the estimated critical values (Table 2). In these cases no formation of Sr- and Ba-oxalates is expected, and the biodynamics of Sr and Ba therefore should deviate considerably from that of Ca,

contrary to what is actually found. However, Sr and Ca are known to form mixed oxalates (Gmelin 1960), meaning that Sr is always coprecipitated with Ca-oxalate, irrespective of its concentration. This coprecipitation explains the similarity of Ca and Sr over the whole concentration range of Sr. Since Ba shows larger deviations from Ca than Sr does (Fig. 2), the formation of mixed Ba-Ca-oxalates by coprecipitation seems to be less pronounced, thus leaving more possibilities for the slightly different characteristics of the ions to influence their respective accumulation behaviour. The observed decrease of Ba/Ca with the AC (Tables 4, 5), the larger values of λ (Ba) than of λ (Ca) (Table 6) and the smaller values of Ba₄/Ba₁ than of Ca₄/Ca₁ (Table 7) all suggest a somewhat larger retranslocation of Ba than of Ca.

Mn at low concentrations

With Mn, contrary to Sr and Ba, there is a concentration range where its biodynamics are completely different from that of Ca. Trees with Mn₁ < 50 µg/g have decreasing concentrations (Fig. 3), whereas Ca in the same trees increases strongly with time. Published data on Mn in conifer needles mostly indicate an increase, but there are also some reports of decreasing concentrations (Nilsson 1972; Anonymous 1986; Horak and Zvacek 1987), usually related to small Mn values as in the present investigation. This varying behaviour of Mn (increasing or decreasing) is also reflected by the inconsistent and vague rating of its phloem mobility. Mn is said to be “apparently immobile as Ca” (Lange et al. 1987), “intermediate” (Marschner 1986), “seems to be partially mobile” (Clarkson and Hanson 1980) or “relatively mobile” (Ziegler 1975). In this context it is important to note that the function fitted to low Mn concentrations (Eq. 2) is identical to the one that describes Rb and Cs in all trees (Tobler et al. 1994). Figure 3 compares the behaviour of Mn and Rb at REG; it is obvious that both elements change basically in the same way; Cs (not shown) changes exactly as Rb. The ions of Rb and Cs are spherical with low polarizability and their reactions are predominately ionic. They also do not form insoluble compounds in plants and can thus be considered prototypes of mobile cations. From the similarity of the biodynamic functions of Rb, Cs and Mn it may be concluded that Mn in the low concentration range is entirely phloem mobile and that it has a correspondingly large retranslocation.

As stated, Mn also forms oxalates, but its solubility is larger than that of Ca, Sr and Ba. Indeed the concentration range where Mn was found to be mobile is below the estimated critical value of 100 µg/g. Obviously Mn at low concentrations does not form mixed oxalates with Ca and thus escapes coprecipitation with the Ca-oxalate. That the observed free mobility of Mn is not due to a lack of the precipitating agent oxalic acid is shown by the fact that in the same trees there is a strong increase of Ca with time and therefore an abundant formation of Ca-oxalate (Fig. 1, curve A2). If we compare the dynamic behaviour of Mn and Ca as a function of Mn₁, we note an increasing similarity in trees with Mn₁ > 100 µg/g (Fig. 2d), ob-

viously because an increasing part of the Mn is precipitated as oxalates as is most of the Ca. An almost complete congruency between Mn and Ca is only reached in trees with Mn₁ greater than about 300 to 500 µg/g, where Mn is far above its estimated solubility value.

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