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Similar patterns of change in stemwood calcium concentration in red spruce and Siberian fir

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Abstract. Changes in stemwood calcium concentration ([Ca]) for the last 120 years occurred in a common pattern for two sample collections of red spruce ($n = 33$ and 20) from the northeastern United States and for one sample collection of Siberian fir ($n = 20$) from southcentral Siberia, Russia. The [Ca] was measured for wood formed during the periods 1871–90, 1891–1910, 1911–30, 1931–50, 1951–70 and 1971–90. For each core, the relative increase or decrease in [Ca] for adjacent periods of wood formation was recorded. The relative frequency of positive change in [Ca] for each period of wood formation was calculated for the three sample collections.

Previous research indicated that under equilibrium conditions, [Ca] in stemwood tended to decrease in more recently formed wood, due to declining numbers of Ca binding sites. Consequently, we expected a low frequency of positive changes in [Ca] in successively formed wood. Consistent with expectation, the relative frequency of positive change from the preceding period to the periods 1891–1910, 1911–30, 1931–50, and 1971–90 were low. Contrary to expectation, the frequency of positive increases in [Ca] more than doubled in 1951–70 compared to 1931–50. The frequency of positive increases in the 1951–70 period relative to the preceding period was 48%, significantly greater than all other periods ($P \leq 0.01$). The frequencies of positive increases for all other periods were not significantly different from each other (overall mean = 21%, SD = 7).

This anomaly in the frequency of positive change in [Ca] in wood formed in 1951–70 relative to wood formed in 1931–50 indicated a perturbation in the ion exchange chemistry of stemwood in two widely separated parts of the northern coniferous forest. This anomaly could be due to external or internal factors. Changes in sap chemistry that affected stemwood chemistry could have been due to changes in the rooting zone. Such changes in rooting zone chemistry could result from the atmospheric deposition of ionic pollutants. Other external factors that could cause the observed anomaly include unusual climatic periods or environmental disturbances such as logging or fire. Internal factors that might produce an anomalously high frequency of positive change of [Ca] include heartwood formation, stemwood infection and a hypersensitive response of the tree against infection.

Key words. Dendrochemistry, forest decline, environmental markers, wood cations.

INTRODUCTION

Declining health, productivity and diversity of some northern forest types has been linked to the rapid increase in emissions of oxides of sulfur and nitrogen (Fig. 1). The deposition of these pollutants shifts the chemical equilibrium of the soil rooting zone (Bondietti, Baes & McLaughlin, 1989). Northern coniferous forests are especially sensitive to the deposition of strong acid anions such as nitrate and sulphate (Tomlinson, 1990). Sensitivity to deposition is greatest where essential cation storage and uptake is from ion exchange sites in thick, well-defined forest floor or humus (Shortle & Bondietti, 1992). The input of strong acid anions such as nitrates and sulphates tend to mobilize both essential base cations (e.g. Ca and Mg) and cations that are antagonistic towards essential base uptake (e.g. Al). Mobilization beyond the immediate needs of plant uptake results in the leaching of essential bases out of the rooting zone. The quantity of essential base in the forest floor is limited. Unfortunately, the natural availability of Al is essentially inexhaustible. As the proportion of exchangeable Al increases with respect to exchangeable Ca in the rooting zone, forest stands may enter into decline due to suppressed growth and increased vulnerability to pests and pathogens (Shortle & Smith, 1988).

Previous research with red spruce (*Picea rubens* Sargent) developed the scenario that forest decline may be due to the deposition of strong acid anions through an aluminum-induced calcium deficiency syndrome (Shortle & Smith, 1988). Although differing in certain aspects, what may be an analogous decline in Norway spruce (*Picea abies* (L)

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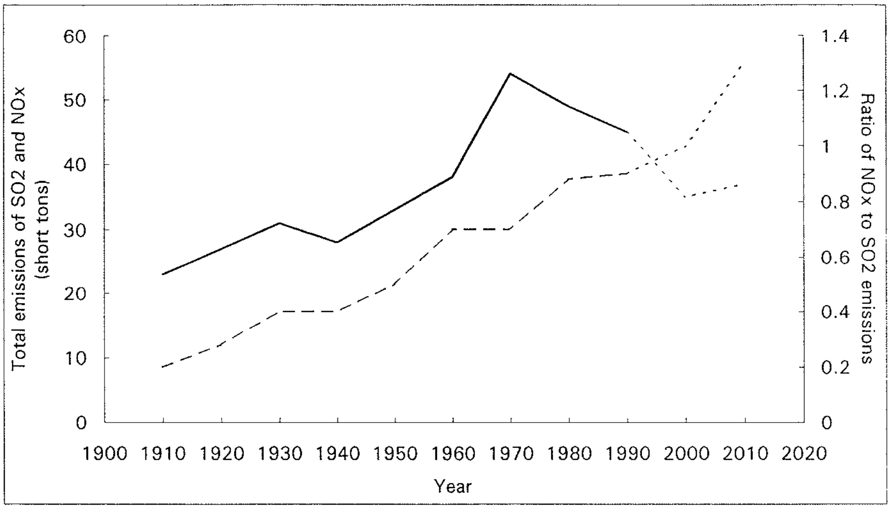

FIG. 1. Temporal trends in emissions of SO_2 and NO_x in the United States. Total emissions are indicated by the solid line and the ratios of NO_x to SO_2 emissions are indicated by the bold broken line. Estimates for future emissions are indicated by the dotted lines (derived from NAPAP, 1992).

Karsten) was attributed to a nitrogen-induced magnesium deficiency (Schulze, 1989). Comparisons of historical to current concentrations of essential bases in coniferous forest floors supported the hypothesis that cation mobilization and leaching had occurred since the middle of this century at locations throughout the northern coniferous forest in both North America and Europe (Shortle & Bondietti, 1992). A preliminary examination of radial trends of cation concentration in the stemwood of red spruce and other forest species in the northeastern United States suggested that a signal of cation mobilization had been recorded in stemwood (Bondietti *et al.*, 1990).

This research examines and compares the radial trends of calcium concentration in red spruce from the northeastern United States and Siberian fir (*Abies sibirica* Ledebour) in southcentral Russia. Calcium was emphasized because it is the base element most required for tree growth and that Ca availability in these forest soils may be potentially deficient. The two species were chosen as being important components of potentially sensitive forest types. The two regions selected were as widely separated as possible while still being similar habitats.

MATERIALS AND METHODS

We analysed three sets of data on the concentration of Ca in the stemwood of northern conifers. The first data set, NE1, was derived from a previously published report (Bondietti *et al.*, 1990) of divalent cation concentration in red spruce grown in the northeastern USA (Fig. 2). The data in NE1 were obtained through various methods of sample acquisition, preparation and analysis. Data trends from most of the individual trees in NE1 were not available. However, published data summaries allowed comparison with the other two data sets in this investigation. The second data set, RU1, was prepared from samples of Siberian fir collected from the Sayan Mountains of the southern Krasnoyarsk region of Russia (*ca.* 53°N lat., 93°E long.) in August, 1991 (Fig. 2). The third data set, NE2, was prepared from samples of red spruce collected from Big Moose Lake, New York, Cone Pond and Crawford Notch, New Hampshire, and Kossuth, Maine in the Adirondack–New England highlands of the USA (*ca.* 44°N lat., 69–74°W long.) in June 1992 (Fig. 2). We used the same methods of sample collection and analysis for RU1 and NE2. For RU1 and NE2, we used an increment borer (12 mm i.d.) to remove stem cores from mature, canopy trees (30–60 cm d.b.h.) at 130 cm above ground-line. Cores were placed on racks to dry on the same day that they were collected.

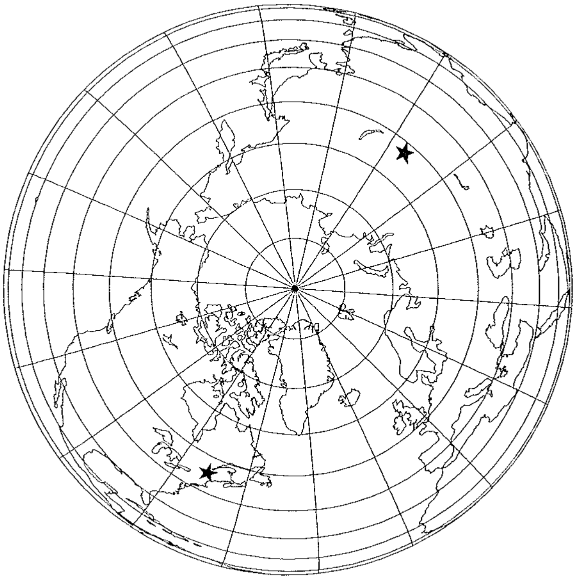

FIG. 2. Polar projection map of the northern hemisphere. The locations of data set NE1 and NE2 in the north eastern United States (lower star) and data set RU1 in south central Russia (upper star) are indicated.

TABLE 1. Analysis of variance of transformed frequencies of positive change of calcium concentration in conifer stemwood[1].

Source of variation	Sum of squares	d.f.	mean square	F	P value	F-critical ($P = 0.01$)
Successive periods	0.283	4	0.071	14.9	< 0.001	5.99
Error	0.047	10	0.005			
Total	0.330	14				

[1] The frequency of positive change in Ca concentration for successive bidecadal periods was compared following arcsin-square root transformation.

For chemical analysis, we selected single cores from five trees from each of four locations within the sampling areas of RU1 and NE2. Selected cores were free of knots, pitch and visible indicators of previous injury or infection. Air-dried cores were glued into grooved wooden blocks and sanded with a series of successively finer grits. Following sanding, ring widths were measured and ring width series were crossdated. Decadal periods of ring formation were marked on the block surface, adjacent to the mounted core.

Minocha & Shortle (1993) described the preparation, extraction and analysis of increment cores for cation concentration. In brief, we removed drill shavings from each mounted core with a 3.2 mm Ti-coated twist drill bit (Fig. 3A). We drilled perpendicular to the transverse surface at the middle of each decadal growth period (Fig. 3B). Because of the variable width of growth rings and the fixed diameter of the bit, samples contained varying numbers of years of growth within the fixed decadal limits. In a few instances in which growth rings were very narrow, shavings from a single drill hole contained wood formed during two decadal periods. Periods of suppressed, juvenile growth at the tree centres were not sampled. We processed 30 mg of wood shavings for cation analysis from each drill hole. Each sample was extracted in 6 ml of 0.01 M HCl for three freeze–thaw cycles (Minocha & Shortle, 1993). The concentration of Ca was determined by direct-coupled plasma emission spectroscopy. Each concentration was considered as the concentration for that decadal period of growth. In order to visualize the trend for each core, the concentration of Ca was plotted against the period of wood formation.

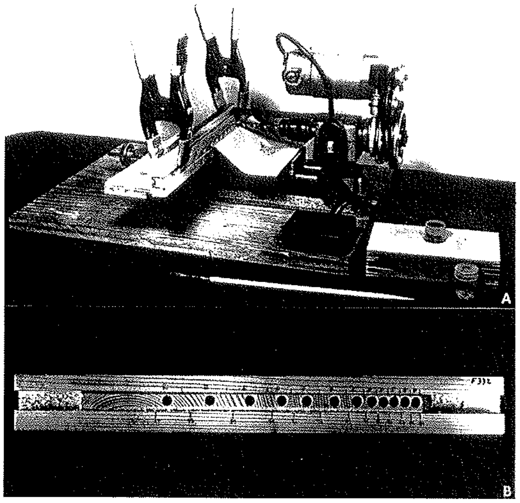

FIG. 3. (A). Apparatus for removing wood samples for chemical analysis from increment cores. The mounted core is clamped to a movable stage. The stage, attached to a threaded rod, is pressed against the turning drill bit. Drill shavings are collected on the filter paper beneath the core and drill bit. (B). An increment core after the removal of samples. Sample positions are centered in the middle of each decade of wood formation. As ring width varied and sample volume was fixed, the spacing of the sample holes and the number of rings contained in each sample were variable.

Previous research showed a trend of decreasing Ca concentration with increasing radius in the stemwood of red spruce (Momoshima & Bondietti, 1990). Consequently, we expected a comparatively high frequency of decreasing Ca concentration in wood formed in successively more recent time periods. In order to support this expectation or to detect a departure from this trend, the frequency of increased Ca concentration in successively formed wood was calculated for all three data sets: NE1, RU1 and NE2. Comparisons between adjacent bidecadal periods were chosen to lessen the effect of decadal variability and to compensate, in part, for the width of conducting sapwood during the growth of the tree. The mean concentrations within each core were calculated for the periods 1891–1910, 1911–30, 1931–50, 1951–70, and 1971–90. Following arcsin-square root transformation, the frequency of increased Ca concentration was analysed by oneway ANOVA with each adjacent pair of bidecadal periods considered as a treatment (total of four treatments) and each data set as a replicate ($n = 3$). When justified by a significant F-test ($P < 0.01$), mean frequencies were compared by Fisher's protected LSD test.

RESULTS

Most increment cores of both red spruce and Siberian fir showed a decreasing radial trend in Ca concentration (Figs 4, 5). Superimposed on some of the trends of decreased concentration were periods of increased Ca concentration. The frequency pattern of positive change in bidecadal mean concentration of Ca was similar for NE1, RU1 and NE2 (Fig. 6).

The frequency of increased Ca concentration from the 1931–50 period to the 1951–70 period (48%) was significantly greater than for all other comparisons of successive bidecadal periods of wood formation ($P \leq 0.01$ Table 1). The frequency of positive increases for all other comparisons of adjacent bidecadal periods were not significantly different from each other (overall mean = 21%, SD = 7).

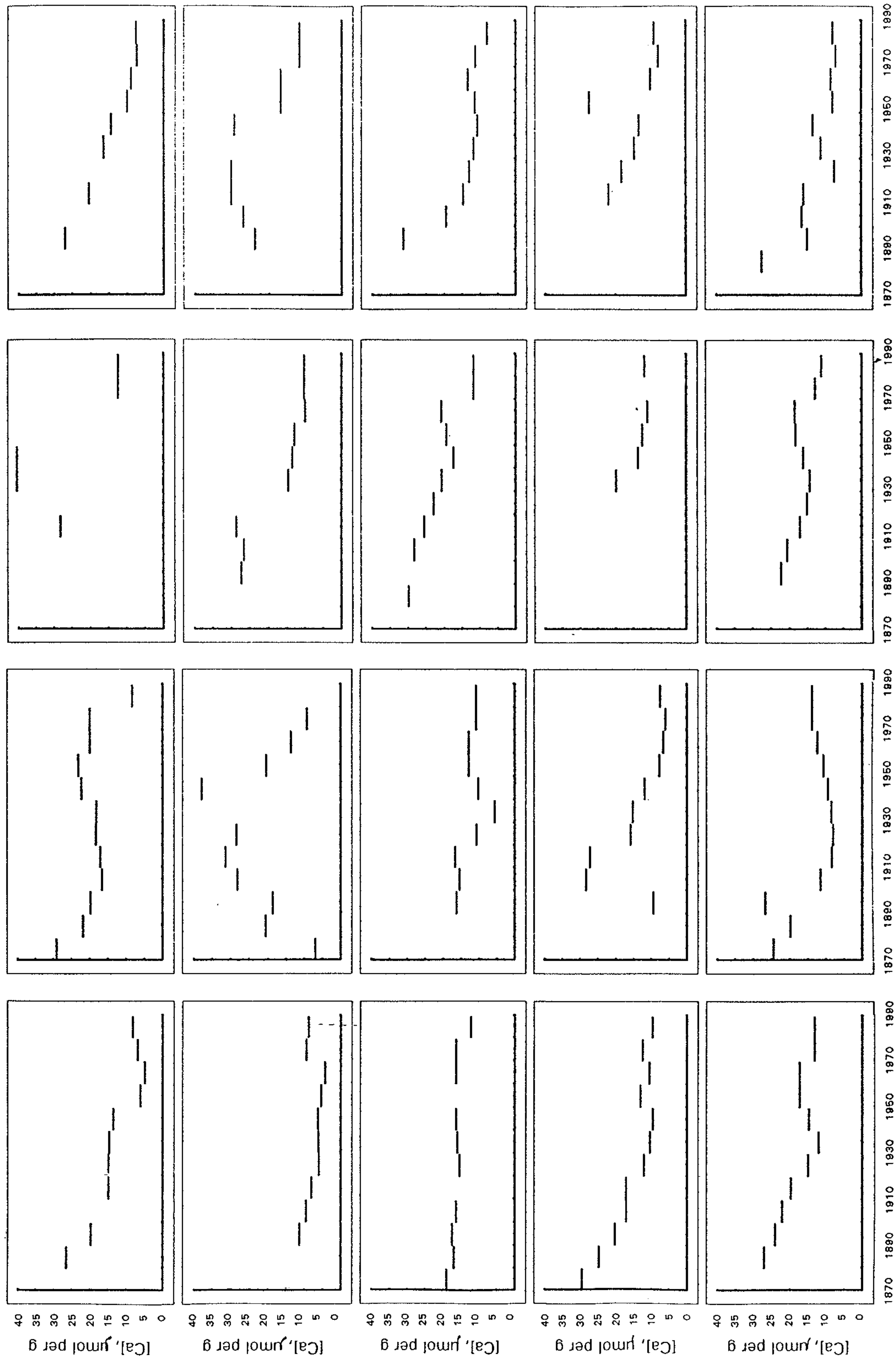

FIG. 4. Radial trends of calcium concentration in wood of Siberian fir (data set RU1). Each graph is the concentration trend for one core. The horizontal length of each line indicates the period of wood formation.

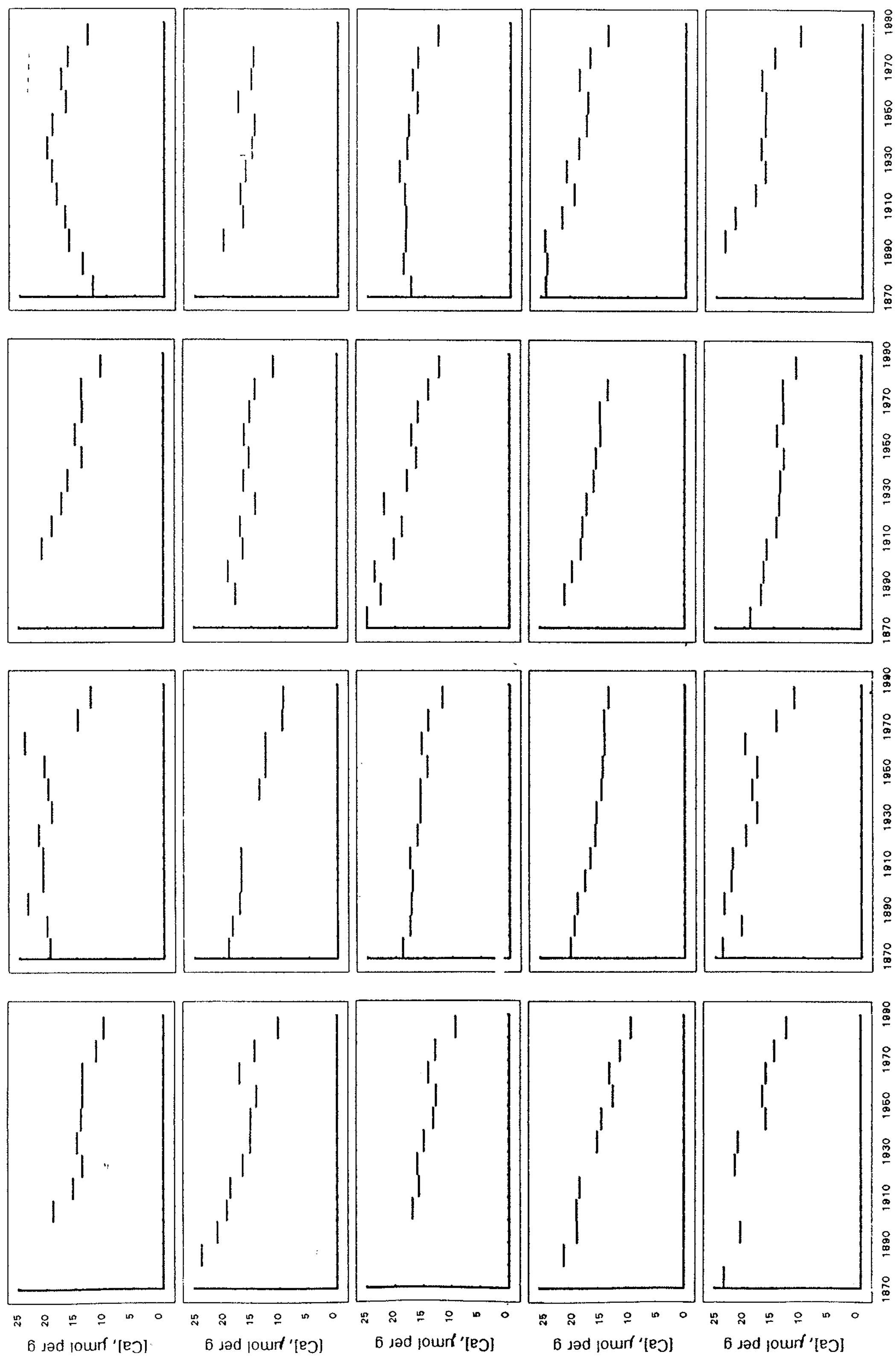

FIG. 5. Radial trends of calcium concentration in wood of red spruce (data set NE2). Each graph is the concentration trend for one core. The horizontal length of each line indicates the period of wood formation.

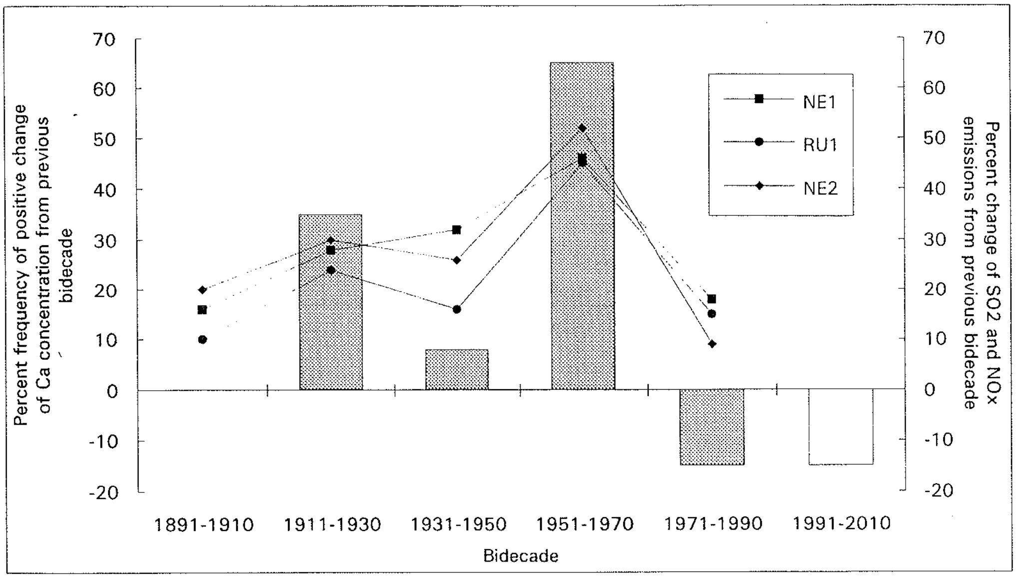

FIG. 6. Temporal change in Ca concentration in stemwood and in SO_2 and NO_x emissions. The plotted lines indicate the percentage frequency of increased Ca concentration ($n = 20$) for the NE1, RU1, and NE2 data sets. The plotted bars indicate the percent change of SO_2 and NO_x emissions (derived from NAPAP 1992). The x-axis contains categories of comparisons between adjacent bidecadal periods. For example, the 1891–10 category represents the change from the 1871–90 period to the 1891–10 period.

DISCUSSION

Red spruce and Siberian fir contain similar anomalies in the radial trends of changes in calcium concentration. The overall trend in most of the increment cores was a decrease in calcium concentration in more recently formed wood (Figs 4, 5). Absolute concentrations of Ca varied from core to core. However, species differences, if present, between red spruce and Siberian fir in the absolute concentration of Ca were too small to be detected by this experiment. The overall trend of decreasing concentration was consistent with previous descriptions of Ca trends (Bondietti *et al.*, 1990; Momoshima & Bondietti, 1990). In red spruce stemwood, Ca occurs as the divalent cation and is bound to ion exchange sites, primarily the anionic carboxylic acid groups of pectins and primary wall materials (Demarty, Morvan & Thellier, 1984). Ion binding experiments with red spruce wood indicated that the number of available ion exchange sites per unit of wood tended to decrease with increasing diameter of the stem (Bondietti *et al.*, 1990). Consequently, when pH and sap concentrations of Ca were constant, the concentration of Ca in stemwood tended to decrease in more recently formed wood. This was the general trend for most of the radial sequences of Siberian fir and red spruce sampled in this experiment (Figs 4, 5).

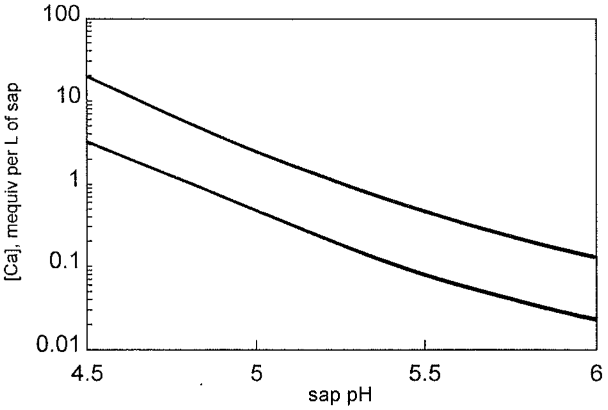

FIG. 7. The relationship in red spruce wood of pH and Ca concentration in the sap to two levels of saturation of ion exchange sites with Ca. Note that the vertical axis of the graph has a common log scale. The upper and lower lines represent 80% and 60%, respectively, of the binding capacity of stemwood for Ca (redrawn from Momoshima & Bondietti, 1990).

The anomaly in this trend of decreasing Ca concentration was the relatively high frequency of increased Ca concentration from the 1931–50 period to the 1951–70 period (Fig. 6). Previous research with red spruce interpreted this increase as a signal of the temporary mobilization of bases in the tree rooting zone (Bondietti *et al.*, 1990; Momoshima & Bondietti, 1990). Such a period of cation mobilization would result from anionic loading of sensitive forest soil with the atmospheric deposition of nitrates and sulphates (Shortle & Bondietti, 1992). The mobilization of chemical bases in the soil that was recorded in the chemistry stemwood was coincident in time with the greatest increase in SO_2 and NO_x emissions (Fig. 6). Finding a similar signal of increased Ca concentration in Siberian fir emphasizes the need to explain this anomaly in radial trends of Ca concentration.

Theoretically, increased Ca concentration in healthy stemwood could be due to increased numbers of ion exchange sites, increased pH, increased concentration of Ca in the tree sap or some combination of these factors. We reject the explanation of increased numbers of ion exchange sites as both direct and indirect evidence shows a trend of decreasing, not increasing number of exchange sites and decreasing Ca concentration (Bondietti *et al.*, 1990; Smith & Shortle, 1995). The relationship of exchangeable Ca in stemwood to Ca concentration and pH of the sap has the characteristics of a Donnan equilibrium in which 60–80% of binding sites are occupied with Ca (Momoshima & Bondietti, 1990). The simplified relationship (Fig. 7) indicated that an increase in saturation of stemwood binding sites with Ca from 60% to 80% can be brought about by either a pH increase from 5.0 to 5.5, or an increase in Ca concentration in the sap from 0.5 to 2.5 mEg/L, or some combination of the two. The relationship shown in Fig. 7 was simplified in that other divalent (e.g. Mg) and monovalent (K) cations would also participate in the chemistry of sap and stemwood. However, the relationship does suggest that sap chemistry changed between the 1931–50 period and the 1951–70 period.

What internal and external factors could change sap chemistry in two widely separated parts of the northern coniferous forest? Potential internal factors include the constitutive transformation of sapwood to heartwood. The sapwood → heartwood boundary was present in the 1951–70 period for essentially all trees in the three data sets. If this maturation process was responsible, we expect that a substantially greater frequency of increased Ca concentration than the observed 48% would have occurred between the 1931–50 period to the 1951–70 period. Also, there is no published reports of accumulation of Ca or increased pH at or near the sapwood → heartwood boundary. The internal, inducible factors that affect wood and sap chemistry include stem infection and the response of trees to injury and infection (Smith & Shortle, 1995). The similarity in timing, pattern and geographical separation argue against a pathological explanation. Base cation mobilization in the rooting zone is an external factor that could increase the frequency of increased Ca concentration. Base mobilization could occur from site disturbances such as fire; however, these sites have no history of fire during this time period. Climatic events that combine the effects of rain and prolonged hot summers can produce a pulse of anions into the soil water, resulting in a mobilization of base cations. However, no such climatic event has been described for these widely separated forests. Base cation mobilization due to the deposition of strong acid anions such as nitrates and sulphates could explain the increased frequency of increased Ca concentration in wood formed in the 1951–70 time period. This is the time period of increased rates of deposition in the north eastern United States (Fig. 1). Pollutant monitoring data for the Sayan Mountain region does not appear to be available. Although this part of Siberia is remote, it is not necessarily free of the influence of regional, industrial pollution.

Because of the legislative response to public concern, total emissions of SO_2 and NO_x have begun to decrease (Fig. 1). However, the extent and severity of damage to forest stands due to previous emissions are not known. The biogeochemical links between emission, deposition, essential element uptake and forest health are not clearly understood. Clearly, some shifts in the biogeochemical equilibrium have occurred, yet it is not clear that a new, stable equilibrium has been reached. In fact, while total emissions of strong acid anions have declined, the ratio of emissions of NO_x to SO_2 have been increasing (Fig. 1). Although nitrogen compounds are essential for tree growth and survival, the deposition of N in soils deficient in base cations can accelerate base depletion, interfere with base cation uptake and result in further forest decline. Such a forest decline has been described for spruce in central Europe (Schulze, 1989).

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