DYNAMICS OF CALCIUM CONCENTRATION IN STEMWOOD OF RED SPRUCE AND SIBERIAN FIR

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Abstract: The atmospheric deposition of strong acid anions such as sulfate and nitrate shifts the ion exchange equilibrium in the rooting zone of sensitive forests. Red spruce and other northern coniferous forests are especially sensitive to deposition due to the shallow rooting of trees in a mor-type forest floor. Initially, the deposition of strong acid ions mobilizes essential cations such as calcium (Ca) from ion-exchange sites on soil organic matter. Hypothetically, this mobilization would result in a brief period of increased availability for root uptake. Evidence for this temporary period of increased uptake of essential Ca is the subject of this report. Radial trends in stemwood calcium concentration [Ca] occurred in a common pattern in two sample collections of red spruce from the northeastern United States and in one sample collection of Siberian fir from south-central Siberia, Russia. The [Ca] was measured in wood segments comprising rings that formed during 1871-90, 1891-1910, 1911-30, 1931-50, 1951-70 and 1971-90. For each core, the relative increase or decrease in [Ca] for consecutive periods of wood formation was determined. Previous research indicated that under equilibrium conditions, [Ca] in stemwood decreased in more recently formed wood due to declining numbers of Ca binding sites. Consistent with expectation, the relative frequency of positive change was low among most consecutive periods of growth. Contrary to expectation, however, the frequency of positive increases (48 percent) in [Ca] doubled in 1951-70 compared to 1931-50; this increased frequency was significantly greater ($P \leq 0.01$) than between all other periods.

INTRODUCTION

Declining health, productivity, and diversity of some northern forests have been linked to the rapid increase in emissions of oxides of nitrogen and sulfur (Fig. 1). Evidence that supports this linkage of pollutant emission and deposition to deterioration in forest condition and stability is indirect and subject to alternate explanations (Friedland and others 1993, Johnson and others 1994, Miller and others 1992, and Schlegel and others 1992).

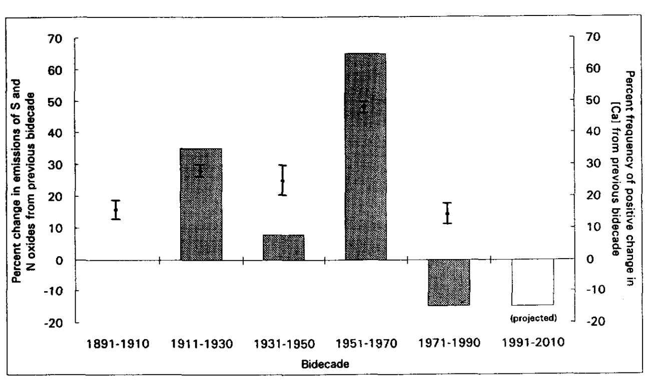

Figure 1. Bars represent percent change in bidecadal mean emissions of S and N oxides (derived from NAPAP 1992). For example, the bar for the 1931-50 bidecade represents an increase in emissions of 25 percent compared to the 1911-30 bidecade. Scatter plots represent the mean percent frequency of positive change in [Ca] from the previous bidecade. Means were calculated from the two data sets of red spruce in the northeastern United States and one data set of Siberian fir from the Sayan Mountains in Siberia, Russia. Each error bar represents the standard error associated with the mean.

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Deposition of strong acid anions such as nitrate and sulfate onto the forest floor tends to mobilize essential base cations e.g., Ca^{+2} and Mg^{+2}, and cations that are antagonistic to the uptake of essential bases, e.g., Al^{3+} (Asp and Berggren 1990; Joslin and others 1988, Kuhn and others 1995). Northern coniferous forests are especially sensitive to the deposition of strong acid anions (Majdi and Persson 1993; Tomlinson 1990). Sensitivity to deposition is greatest where essential cation storage and uptake are from ion-exchange sites in thick, well-defined mor-type forest floor (Cronan 1991). Such mobilization may have three consequences. First, root uptake of essential bases may increase temporarily due to a period of increased availability (Bondietti and others 1990, Shortle and others, in press). A hypothetical marker of increased availability of essential Ca is presented in this report. Second, root uptake of essential bases may decrease due to the antagonistic binding of Al^{3+} to the ion-exchange sites (Johnson and Fernandez 1992; Smith and others, in press). Third, root uptake of essential bases may continue to decrease as essential bases leach out of the forest floor, eventually impoverishing the rooting zone (Federer and others 1989). These consequences may or may not occur in a continuous series, and the sequence may be interrupted or reversed due to the replenishment of essential bases to the forest floor through stand disturbance.

We have proposed an etiological sequence, the aluminum-induced calcium deficiency syndrome, which may place at risk the health and productivity of sensitive spruce-fir forests in the northeastern United States (Shortle and Smith 1988). Our published reports and those of cooperators tend to support the linkage of pollutant deposition, mobilization and depletion of essential bases, and tree response. Preliminary research on several tree species indicated that stemwood sap increased in pH and/or divalent cation concentration in the mid-1900's (Bondietti and others 1990; Momoshima and Bondietti 1990). These changes would be expected during the hypothetical period of enhanced availability due to cation mobilization initiated or enhanced by atmospheric deposition. A comprehensive historical review indicated a marked, widespread decline in essential divalent cations in mor soil of northern forests in the mid- to late-1900's (Shortle and Bondietti 1992). The ratio of Al:Ca in fine root tips, a hypothetical marker of antagonistic conditions in the rooting zone, was greater at higher elevations and in lower layers of the forest floor (Smith and others, in press). New methods for the extraction (Minocha and others 1994) and determination (Minocha and others 1990) of polyamines allowed the evaluation of the usefulness of these growth regulators as markers of stress caused by Al. Cultures of woody plant tissue dosed with Al indicated that both the timing of the dose and the duration of exposure affected cellular processes in a dose-dependent manner (Minocha and others 1992, Zhou and others 1995). Consequently, the effect of mobilization and antagonistic processes may depend on the phenological condition of the tree.

The time course for these consequences of mobilization is not well established. Rates of cation mobilization and depletion of essential bases differ among forest locations. We do know that the concentration and total amounts of essential bases 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 begin to decline due to suppressed growth and increased vulnerability to pests and pathogens (Shortle and Smith 1988).

This report presents data on the dynamics of changes in radial trends of calcium concentration [Ca] in stemwood of red spruce from the northeastern United States and Siberian fir (*Abies sibirica* Ledebour) from south-central Siberia, Russia. The [Ca] in these trees have been published (Shortle and others, in press). Ca was emphasized because it is the base element most required for tree growth, and Ca availability in these forest soils may be potentially deficient. The two species were chosen as important components of potentially sensitive forest types. The two regions selected were as widely separated as possible while still being similar habitats.

METHODS

We analyzed the [Ca] in stemwood of three groups of northern conifers. The first data set, NE1, was derived from a previously published report (Bondietti and others 1990) on divalent cation concentrations in red spruce (n = 33 trees) from the northeastern United States (Fig. 2). Data in NE1 were obtained through various methods of sample acquisition, preparation, and analysis. Trends in [Ca] of most individual trees in NE1 were not available, though published data summaries allowed comparison with the other data sets in this investigation. The second data set, RU1, was from Siberian fir (n = 20 trees) collected in August 1991 from the Sayan Mountains of the southern Krasnoyarsk region of Siberia, Russia (ca. 53°N, 93°E) (Fig. 2). The third data set, NE2, was from red spruce (n =

20 trees) collected in June 1992 from Big Moose Lake, New York, Cone Pond and Crawford Notch, New Hampshire, and Kossuth, Maine, in the Adirondack-New England highlands (ca. 44°N, 69-74°W) (Fig. 2).

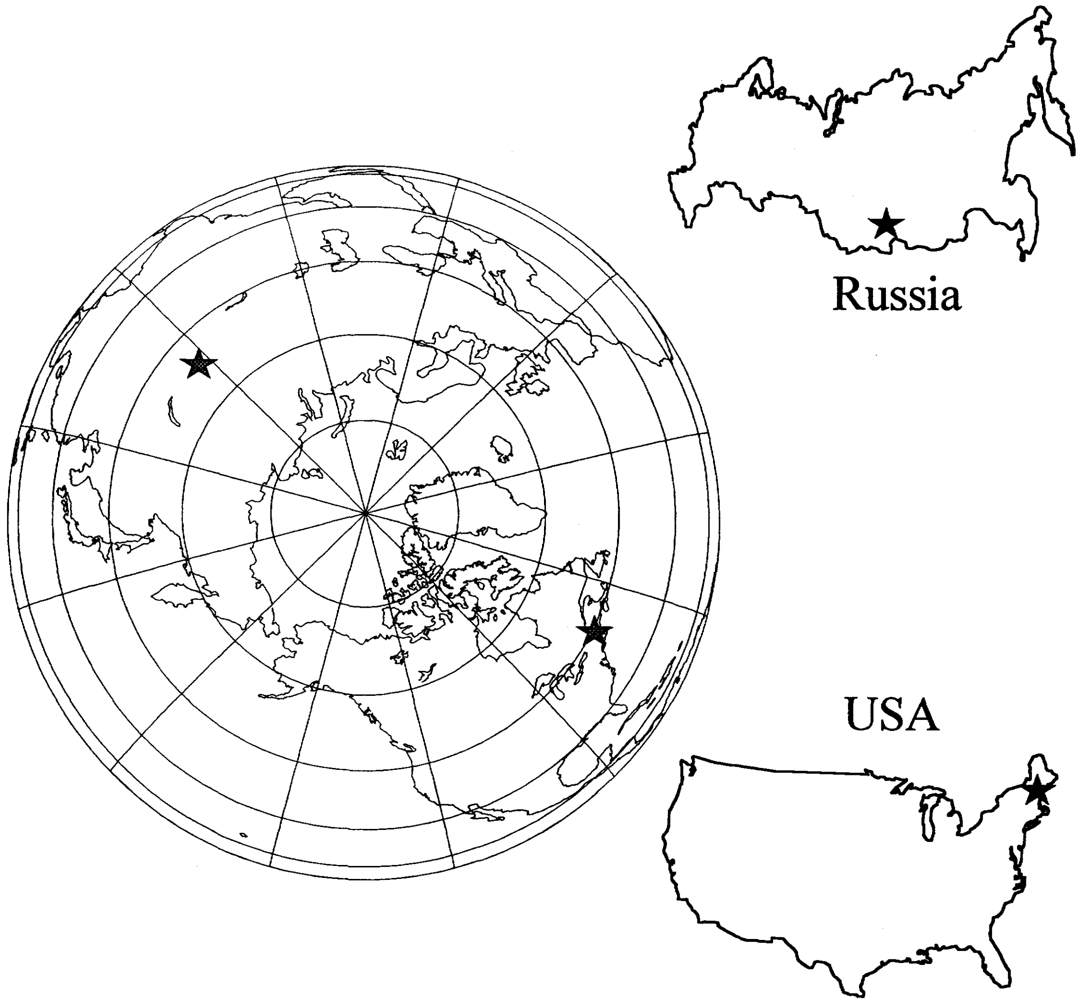

Figure 2. Polar and Mercator projection maps showing the locations of data sets NE1 and NE2 in the northeastern US and data set RU1 in south-central Siberia, Russia.

For RU1 and NE2 we used identical methods of sample collection and analysis. We removed stemwood cores with an increment borer (12 mm inside diam.) from mature, canopy trees (30 to 60 cm d.b.h.) at 130 cm above groundline. Cores were placed on racks to airdry on the day they were collected. 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 crossdated. Decadal periods of ring formation were marked on the block surface adjacent to the mounted core. Minocha and Shortle (1993) described the preparation, extraction, and analysis of increment cores for cation concentrations. Shavings were removed from each mounted core with a 3.2 mm Ti-coated twist bit drilled perpendicular to the transverse surface at the middle of each decadal growth period. Because of the variable width of growth rings and the fixed diameter of the bit, samples contained varying numbers of growth rings within the fixed decadal limits. Periods of suppressed, juvenile growth at tree centers were not sampled. Thirty mg of wood shavings from each drill hole were extracted in 6 ml of 0.01 M HCl for three freeze-thaw cycles (Minocha and Shortle 1993). The [Ca] was determined by direct-coupled plasma emission spectroscopy. Each concentration was considered as the concentration for that decadal period of growth. Mean concentrations within each core were calculated for 1891-1910, 1911-30, 193-50, 1951-70, and 1971-90. 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. For each core, the [Ca] in successive bidecadal periods were scored as having increased, decreased, or remained the same relative to the preceding period. Previous research showed a trend of decreasing [Ca] with increasing radius in the stemwood of red spruce (Momoshima and Bondietti 1990). Consequently, we expected a comparatively high frequency of decreasing [Ca] in wood formed in successively more recent time periods. To test this expectation, the percent frequency of increased [Ca] in successively formed wood was calculated for NE1, RU1, and NE2. Prior to statistical analysis, the percent frequencies were converted using the arcsin-square root transformation to normalize the distribution and stabilize the variance (Bartlett 1947). The transformed percent frequencies of increased concentrations were analyzed by one-way ANOVA. Each adjacent pair of bidecadal periods was 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

The [Ca] tended to decrease along the stemwood radius for most increment cores of both red spruce and Siberian fir (Figs. 3-4). Superimposed on some of the trends of decreased concentration were periods of increased [Ca]. The frequency pattern of positive change in bidecadal mean [Ca] was similar for all three data sets (Fig. 1).

The frequency of increased [Ca] for 1931-50 period to 1951-70 period (48 percent) was significantly greater than for all other comparisons of successive bidecadal periods of wood formation ($P \leq 0.01$, Table 1). The frequencies of positive increases among all other adjacent bidecadal periods did not differ significantly (overall untransformed mean = 21 percent, SD = 7).

Table 1. Transformed mean frequencies of positive change in Ca concentration in conifer stemwood

Bidecade[a]	Mean[b]	Standard deviation
1891-1910	0.399	0.072
1911-1930	0.553	0.036
1931-1950	0.516	0.096
1951-1970	0.762	0.031
1971-1990	0.378	0.084

[a]The value for the 1891-1910 bidecade represents the frequency of increased [Ca] from 1871-90 to 1891-1910.

[b]Raw frequencies of increased [Ca] for the NE1, NE2, and RU1 data sets were converted with the arcsin-square root transformation prior to statistical analysis. The frequency of increased concentration for the 1951-70 bidecade was significantly greater than for all other periods ($P < 0.01$, Fisher's protected lsd = 0.178). There were no significant differences for other comparisons.

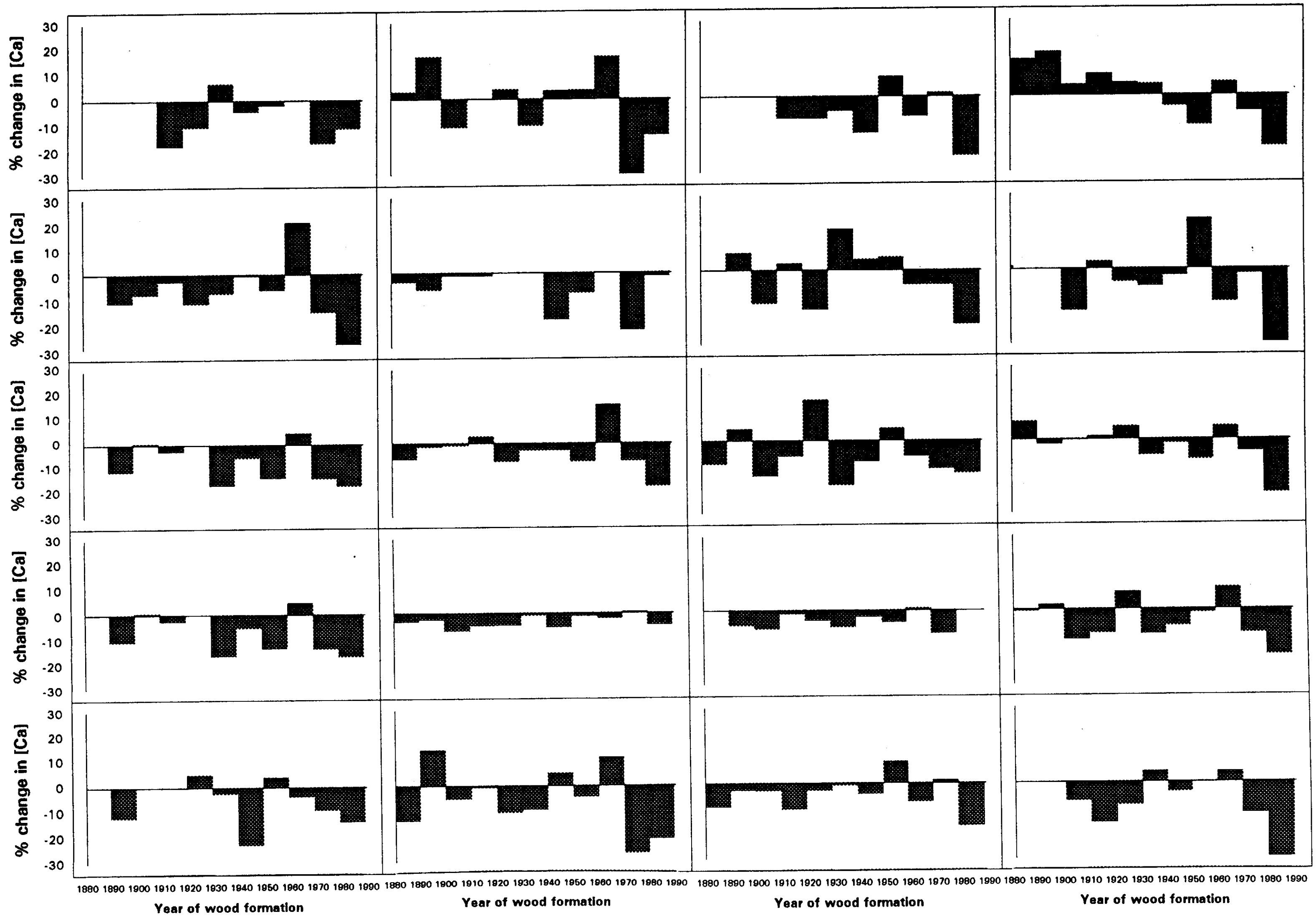

Figure 3. Decadal change in [Ca] in stemwood of red spruce (dataset NE2). For example, the bar for 1950 represents the percent change in [Ca] from 1940 to 1950.

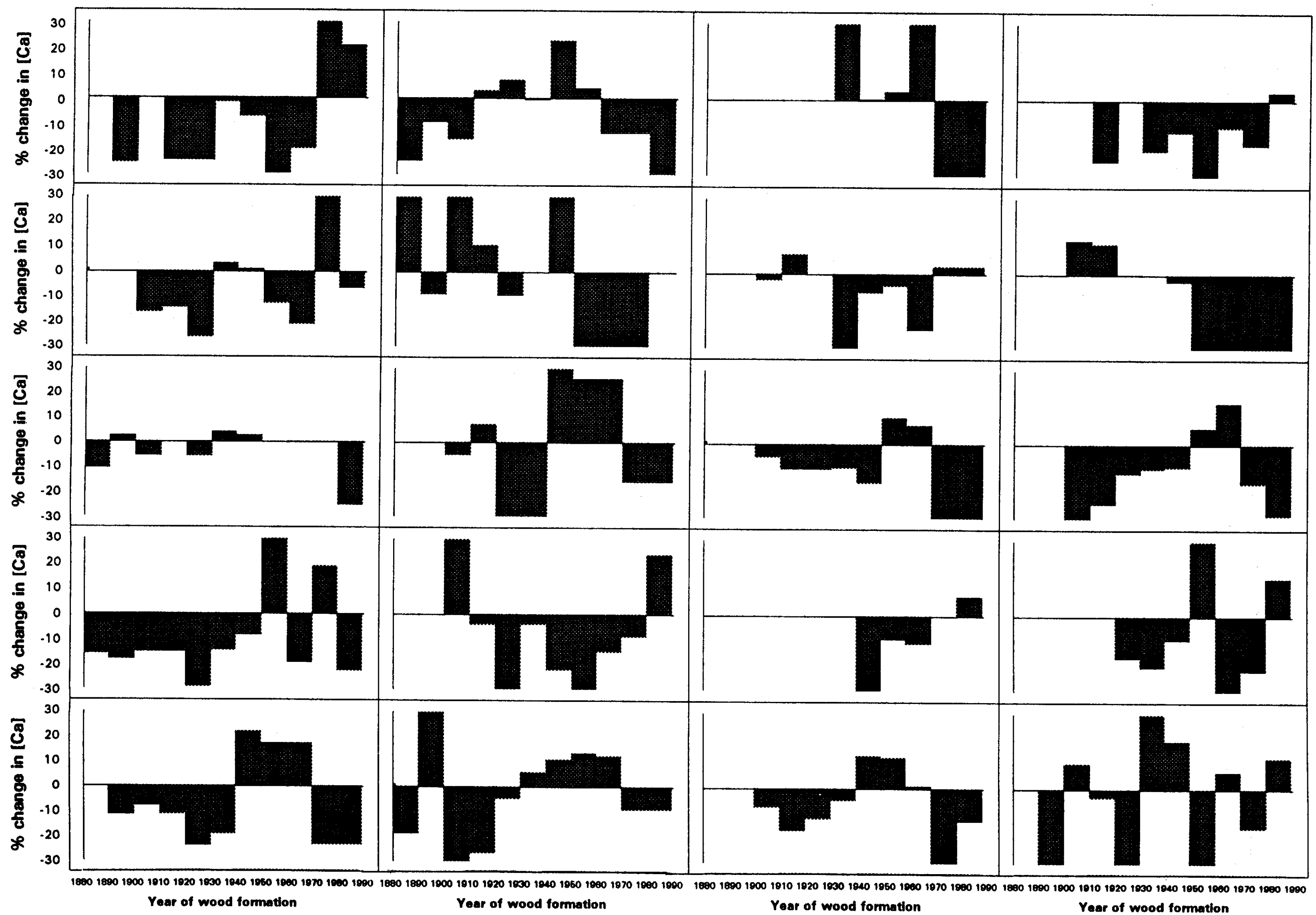

Figure 4. Decadal change in [Ca] concentration in stemwood of Siberian fir (data set RU1).

DISCUSSION

Stemwood samples of red spruce and Siberian fir contained similar anomalous increases in [Ca]. The overall trend in most increment cores was a decrease in concentration in more recently formed wood (Figs. 3-4). This general trend was consistent with ion-exchange characteristics previously described for red spruce (Bondietti and others 1990, Momoshima and Bondietti 1990). In wood, Ca occurs as a divalent cation bound to ion-exchange sites, primarily anionic carboxylic acid groups of pectins and primary-wall materials (Demarty and others 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 stem diameter (Bondietti and others 1990). Consequently, when pH and [Ca] in sap were constant, [Ca] in stemwood decreased in more recently formed wood. The underlying mechanism for the progressive decrease in ion-exchange sites has not been established.

The exception to the trend of decreasing [Ca] was the relatively high frequency of increased concentrations within the 1951-70 rings relative to those formed from 1931 to 1950 (Fig. 1). Previous research with red spruce interpreted this increase as a signal of the temporary mobilization of bases in the tree rooting zone (Bondietti and others 1990; Momoshima and Bondietti 1990). Such a period of cation mobilization would have been expected to result from anionic loading of sensitive forest soil with the atmospheric deposition of nitrates and sulfates (Shortle and Bondietti 1992). The mobilization of chemical bases in soil that was recorded in stemwood chemistry was coincident in time with the greatest increase in SO_2 and NO_X emissions (Fig. 1). The presence of a similar signal of increased [Ca] within Siberian fir emphasizes the need to explain this anomaly more fully in future research.

Hypothetically, [Ca] in healthy stemwood could increase due to increasing numbers of ion-exchange sites, increasing the pH of sap or of [Ca] in the xylem stream, or some combination of these. We reject the explanation of increased numbers of ion-exchange sites as all evidence shows decreasing numbers of exchange sites along the stemwood radius (Bondietti and others 1990; Smith and Shortle, in press). The concentration of exchangeable Ca in stemwood relative to the [Ca] and pH of the sap has the characteristics of a Donnan equilibrium in which 60 to 80 percent of binding sites are occupied with Ca (Momoshima and Bondietti 1990). An increase in saturation of stemwood binding sites with Ca from 60 to 80 percent can be achieved by an increase in pH from 5.0 to 5.5 or an increase in [Ca] in the sap from 0.5 to 2.5 mequiv per L, or combinations of the two. This relationship is complicated somewhat in that other divalent, e.g., Mg, and monovalent (K) cations also participate in the chemistry of sap and stemwood. Nevertheless, the higher [Ca] within wood formed during 1951-70 relative to the previous 20 years suggest a concomitant change in sap chemistry.

What internal or external factors could account for changes in sap chemistry in two widely separated parts of the northern coniferous forest (Smith and Shortle, in press)? Potential internal factors include the constitutive transformation of sapwood to heartwood. The sapwood:heartwood boundary was present in 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] than the observed 48 percent would have occurred between the periods of 1931-50 and 1951-70 period. Also, there are no published reports of the accumulation of Ca or increased pH at or near the sapwood:heartwood boundary in any species of spruce or fir. The internal, inducible factors that affect wood and sap chemistry include stem infection and the response of trees to injury and infection (Smith and Shortle, in press). The similarity in timing, pattern, and geographic separation argues against a common pathological explanation. Base-cation mobilization might increase the concentrations of Ca available to roots, resulting in increased concentrations within wood. Such mobilization could occur from disturbances such as fire, though there are no records of fire on these sites during this time period. Climatic events that combine the effects of rain and prolonged hot summers might produce pulses of anions into the soil water, resulting in mobilization of base cations. However, no such climatic event has been documented for these widely separated forests. Base-cation mobilization due to the deposition of strong acid anions is coincident in time and consistent with known mechanisms that would increase the frequency of increased [Ca] in wood formed in 1951-70. The greatest increase in rates of emissions in the northeastern United States occurred during this period (Fig. 1). Pollution monitoring data for the Sayan Mountain region apparently are not 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 among emission, deposition, essential element uptake, and forest health are poorly understood. Seemingly, some shifts in the bigeochemical equilibrium have occurred, though it is unclear whether a new, stable equilibrium has been reached.

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