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Dendrochemical evidence for soil recovery from acidic deposition in forests of the northeastern U.S. with comparisons to the southeastern U.S. and Russia

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HIGHLIGHTS

- Dendrochemical patterns of Ca, Mg, and K were identified in US and Russian spruce.
- Patterns varied with wood transformations and soil chemistry.
- Patterns were consistent with decreased acid deposition and progressive recovery.

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ABSTRACT

A soil resampling approach has detected an early stage of recovery in the cation chemistry of spruce forest soil due to reductions in acid deposition. That approach is limited by the lack of soil data and archived soil samples prior to major increases in acid deposition during the latter half of the 20th century. An alternative approach is the dendrochemical analysis of dated wood to detect temporal changes in base cations back into the 19th century. To infer environmental change from dendrochemical patterns of essential base cations, internal factors that affect cation chemistry such as the maturation of sapwood and the spread of wood infection need to be recognized. Potassium concentration was a useful marker of these internal maturation and infection that could affect the concentration of essential base cations in wood. Dendrochemical patterns in samples of red spruce in the eastern United States and Norway spruce in northwestern Russia were used to determine how internal changes in base cations can be separated from external changes in root-zone soil to date major changes in the availability of essential base cations associated with a changing environment.

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1. Introduction

Due to naturally high acidity and low base saturation of forest soil, red spruce (*Picea rubens* Sarg.) in the eastern United States and Norway spruce (*P. abies* L. (Karst.)) in northern Europe were particularly vulnerable to adverse effects of acidic deposition derived from industrial emissions (Tomlinson and Tomlinson, 1990). Acidic deposition tended to mobilize essential base cations, deplete the rooting zone, and increase stress for some tree species (Shortle and Smith, 2015).

The rate of emission increase of S and N oxides peaked in the 1960s, gradually decreased during the 1970s and 1980s as the 1970 Clean Air Act was implemented (NAPAP, 1993), and continued to trend downward in the US as the 1990 Amendment to the Clean Air Act was implemented (NAPAP, 2005). The chemical comparison of forest soils in the northeastern US and eastern Canada sampled in the 1980s-1990s and resampled in 2003–2014 indicated an early stage of reversal of the adverse effects if acidic deposition (Lawrence et al., 2015).

The resampling approach to detect changes in the root environment prior to the rapid increase of acidic deposition in the 1960s-1970s is limited by the lack of soil data and archived soil samples. However, dendrochemical analysis of dated wood has the potential to detect major changes in base cations well back to the early 19th century. Dendrochemical patterns integrate cation availability with internal processes of maturation and infection.

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Base cation movement follows a modified Donnan model of cation exchange along the flowpath from soil storage, root uptake, and stem translocation (Momoshima and Bondietti, 1990; Bondietti et al., 1990; Shortle and Bondietti, 1992; Shortle et al., 1997). The purely biophysical Donnan model is modified through active absorption by living cells, resorption during heartwood formation, and disruption by the internal spread of wound-initiated diseases of wood (Smith and Shortle, 1996; Watmough, 1997; Meerts, 2002; Smith, 2008; Smith and Shortle, 2001; Smith et al., 2009, 2014).

The woody stems of mature healthy spruce contains an outer band of living sapwood that surrounds a core of non-living heartwood. The width of the band of sapwood in terms of radial distance and number of rings varies in part due to ring width. The greater moisture content of sapwood compared to heartwood in freshly collected samples is visible as a dark water-soaked appearance in reflected light (Fig. 1A) and translucence in transmitted light. The transformation of sapwood into heartwood is accompanied by a reduction of wood moisture and K content, the latter due to the withdrawal of the symplast and K-rich parenchymal cytoplasm. Unlike many other conifer species, spruce heartwood formation is not accompanied by the deposition of colored extractive products, making dried sapwood and heartwood similar in appearance.

Extensive research on the electrical characteristics of wood in living trees determined that changes in electrical resistance relative to the outer living sapwood can be used to detect the spread of wood decay in spruce and fir trees (Shortle and Smith, 1987). This ionization occurs rapidly and long before any symptoms of decay are visible (Shortle, 1990) and is primarily related to increased concentrations of K ions (Shortle, 1982; Shortle and Ostrofsky, 1983), with concentrations of Mg and Ca ions increased to a lesser degree. Therefore, the concentration of K in dated wood can be used to detect the transformation of sapwood to heartwood in spruce and to detect the internal spread of wood decay that alters the mineral content of wood during the previsual stage of the decay process and disrupts the radial patterns of base cations used to infer external changes in root-zone soil. The alkaline earth elements Ca and Mg share series 2A of the periodic table and both occur as fixed divalent base cations in trees and forest soil. Translocation of Ca is largely apoplastic, following the bulk flow of xylem sap with ion displacement at exchange sites on the xylem cell walls (Bondietti et al., 1990; Smith and Shortle, 2001).

Comparisons across two distinct regions of the eastern US and a third region in northwestern Russia has the potential to increase understanding of internal and external processes that contribute to dendrochemical patterns. The major objectives of this study were to: (1) determine how differences in the periodic growth rate can affect the dating of a major change in root-available Ca and how it differs from Mg; (2) compare the dendrochemical records of red spruce in the northeastern U.S to those in the southern Appalachians, and to Norway spruce at locations with archived soil data in northwestern Russia; and (3) determine how the dendrochemical record changed from the 1980s to the 1990s as acid deposition decreased and the availability of Ca increased from wood decay following red spruce mortality observed in the late 1970s, 1980s, and early 1990s.

2. Materials and methods

2.1. Sample collection and analysis

Decadal dendrochemical trends for the dominant base cations were determined for canopy-dominant or codominant spruce in the northeastern and southeastern US and in northwestern Russia (Fig. 2). Sampled trees were >30 cm in diameter at breast height. Increment cores (12-mm diameter) were extracted at breast height and the visible boundary between sapwood and heartwood marked in four collections. The northeastern red spruce collection was taken from 11 field locations across northern New York, Vermont, New Hampshire, and Maine in 1992–1993 in conjunction with forest soil analysis (David and Lawrence, 1996; Shortle et al., 1997) and from two additional locations in Waterville Valley, NH, in 1994 (Shortle and Bondietti, 1992). In brief, all northeastern and southeastern US sites were dominated by red spruce. Average tree age ranged from 96 to 175 years. Elevation ranged from 80 to 975 m and all soils were classified as spodosols.

The southeastern red spruce collection was taken at the Great Smoky Mountains National Park in Tennessee and North Carolina in 1995 in the vicinity of previous sampling and chemical characterization of spruce fine-roots (Smith et al., 1995). The northwestern Russian collection of Norway spruce was taken in 2001–2002 from a southern boreal forest of mixed Norway spruce and Scots pine (*Pinus sylvestris*). The Russian terrain was flat and low-lying, east of the Bay of Finland. Soil chemistry was determined at this location and is included in this report. At the two Russian sites (Luga and Lisino), exchangeable Ca and Al were determined for forest soil at depths 0–10 cm and 10–20 cm below the top of the mineral soil. In addition, intact soil monoliths collected in 1926 and 1964 were available to provide soil samples from the same layers as in the 2001–2002 sampling. The archived and newly collected soil samples collected were analyzed together to evaluate changes in soil chemistry over time. Soil methods are presented in Lawrence et al. (2005).

The northeastern red spruce re-sample collection was taken in 2003–2004 from six locations previously sampled for the northeastern red spruce collection, as described above and in Lawrence et al. (2012). The resample collection was made to test the persistence of any dendrochemical trend identified in the 1992–1993 collection and to detect changes that may have occurred due to decay of deadwood that produced Ca-rich organic matter during the decade between samples (Shortle et al., 2012).

For all collections, increment cores were mounted in grooved wood blocks, sanded, and cross-dated. Decadal boundaries of cores free of visible internal defects or indication of wood infection were marked. The radial distance of each decadal band was measured to the outer limit of the sapwood.

The dated wood samples were drilled from each mounted core using a Ti-coated drill bit 0.64 cm in diameter. Cores were drilled towards the center of each decadal band and the resulting shavings were taken as the sample for that decade. Because of variation in ring width, the number of rings contributing shavings varied among decadal samples. For each decade, 25 mg of drill shavings was placed in a 15-mL acid washed glass test tube to which 6 mL of 10 mM HCl was added. Cations were extracted from the shavings in three freeze-thaw cycles (Minocha and Shortle, 1993; Shortle et al., 1997). The extract was filtered with a 45-μm syringe filter and the concentration of the major inorganic cations, Ca, K, Mg, was determined by direct-coupled plasma atomic emission spectroscopy (DCP-AES) from 1991 to 1996, and thereafter by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.2. Sample screening

Increment cores lacking clean decadal bands due to wood defects, visible infection, or elevated K concentration (concentration > outermost sapwood band) were screened out of further analysis. The northeastern red spruce cores collection from 123 trees yielded cores with variable numbers of decadal bands ($n = 14$ in 1840s to $n = 104$ in 1900s, and $n = 123$ from 1910s to 1980s). To compare the effect of sapwood width on the dendrochemical record of decadal bands, the northeastern red spruce collection was subdivided for some

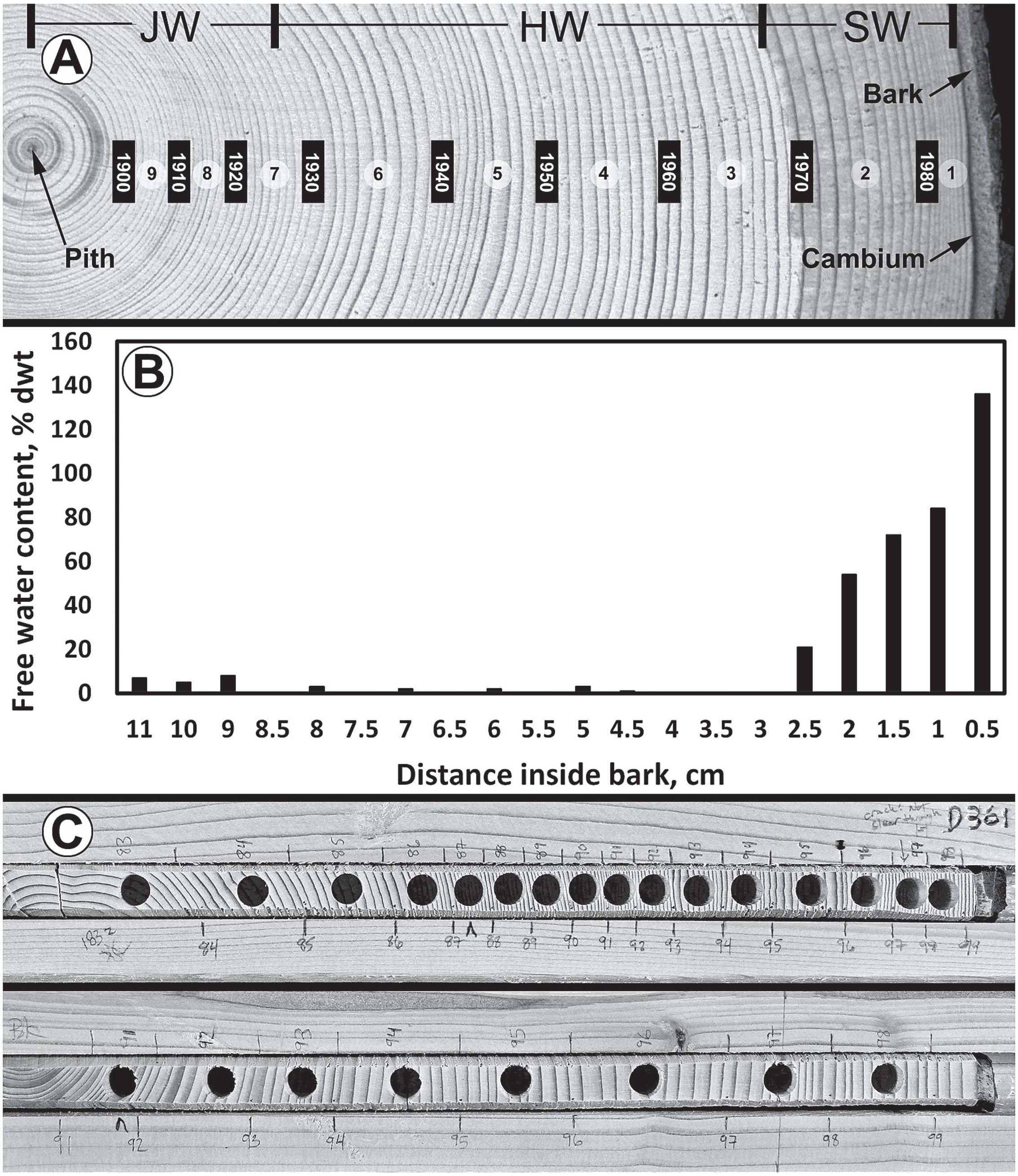

Fig. 1. (A) Freshly cut and sanded red spruce stem section in which decadal bands are marked from juvenile wood (JW) through mature heartwood (HW) to live sapwood (SW), (B) free water content (xylem sap) in a mature spruce tree, and (C) dry 12-mm increment cores from which dated wood samples of decadal bands were drilled (note wider interdecadal spacing in younger, smaller spruce with 8 decadal bands and narrow interdecadal spacing of older, larger spruce with 16 decadal bands).

comparisons to represent older trees with more decadal bands and younger trees with fewer decadal bands of sapwood.

The southeastern red spruce collection yielded 17 cores with decadal bands from the 1840s-1980s ($n = 17$). The initial Russian collection of Norway spruce consisted of 52 cores, 16 of which contained too few decadal bands for analysis, 15 were rejected due to visible symptoms of infection, and an additional 8 were rejected due to elevated K concentration, presumptive evidence of infection. After screening, the Russian collection yielded 13 cores with decadal bands from the 1880s-1900s ($n = 13$). The re-sample collection of northeastern red spruce consisted of 30 cores. Three cores were rejected due to elevated K, yielding a total of 27 cores with decadal band from the 1920–1990s ($n = 27$).

2.3. Identification of significant trends

Data were summarized and compared both in terms of concentration ($mmol \cdot kg^{-1}$) and as interdecadal change in concentration, expressed as a percent. The interdecadal change was calculated as the difference in concentration between successive decadal bands, expressed as a percentage of the concentration of the earlier band and assigned to the later band.

Mean interdecadal changes in concentration of K, Ca, and Mg were tested for statistical significance using a graphical approach (Cumming et al., 2007). In this technique, the mean interdecadal change and associated 95% confidence interval (CI) were calculated for each decade. For cases in which the CI of the mean interdecadal change included zero, no statistical significance was inferred.

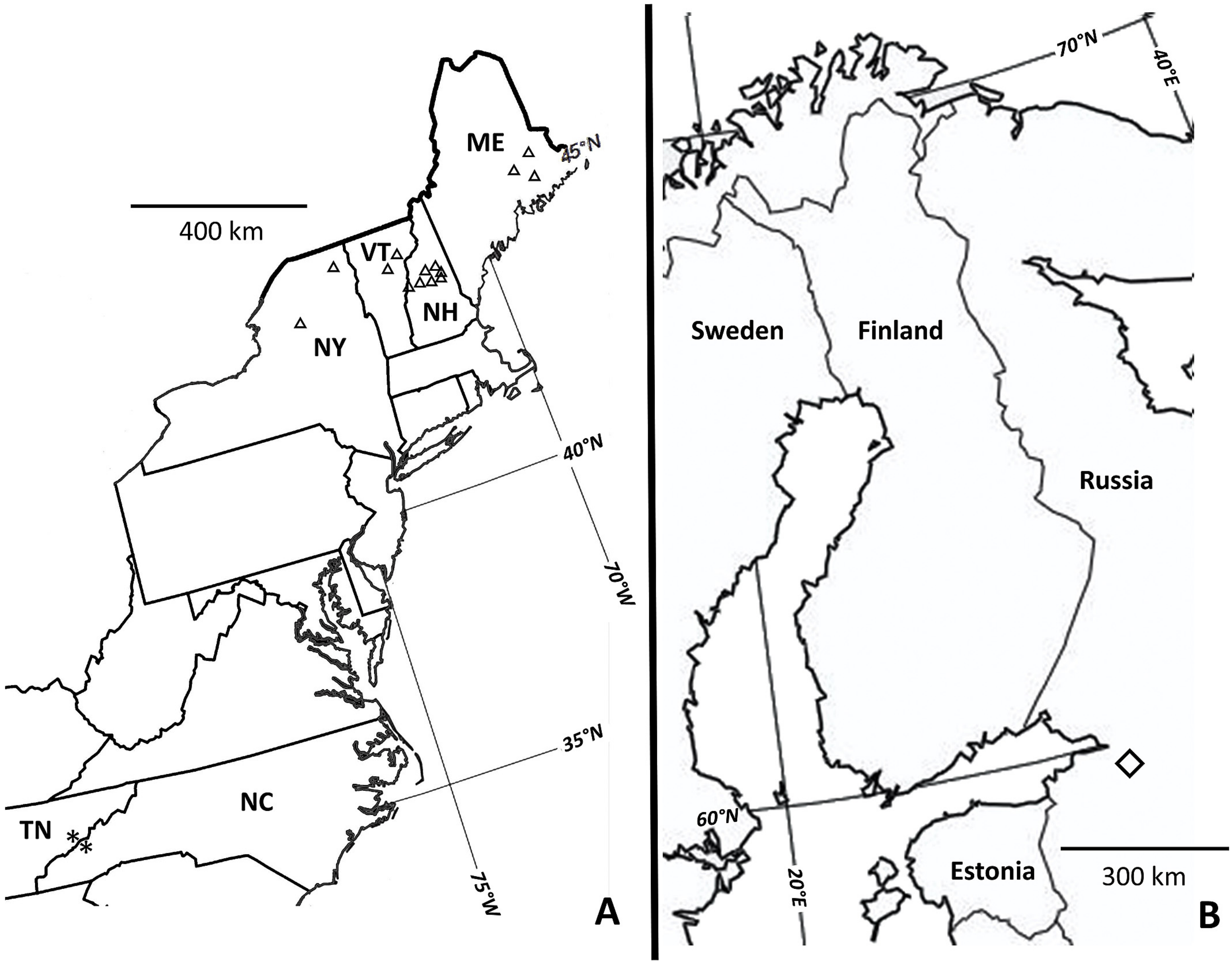

Fig. 2. Location of sampling areas for dendrochemistry. (A) Red spruce were sampled in the northeastern states of New York, Vermont, New Hampshire, and Maine (triangles) and in the southeastern states of Tennessee and North Carolina (stars). (B) Norway spruce were sampled at Luga and Lisino in northwestern Russia, east of the Gulf of Finland (both sites marked by the single diamond).

Significant interdecadal increases or decreases were indicated with a CI range entirely above or below zero, respectively. The statistical significance of mean differences in concentration of K, Ca, and Mg for the same decade in trees at different locations were determined by the degree of overlap of the CI. For $N \geq 10$, statistical significance was indicated by a CI overlap of one-half or less of the length of an error bar arm (Cumming et al., 2007).

To test whether cations in sapwood are retained following the transformation into heartwood or whether the cations are withdrawn or resorbed into the sapwood, the resorption index was calculated as the concentration of each decade divided by the concentration of the outermost sapwood decade. A resorption index value < 1 indicated that the cation was resorbed into sapwood during heartwood transformation. An index value ≥ 1 indicated that the cation was retained by the heartwood or re-introduced by infection.

2.4. Stability of dendrochemical record

The temporal stability or the independence of sampling date on the dendrochemical record was tested for the initial and resampled collection of red spruce. Individual dendrochemical series were grouped by decadal band of peak interdecadal increase in element concentration.

3. Results

3.1. Decadal bands of sapwood and heartwood

Decadal bands were generally more narrow in larger, older trees and wider in smaller, younger trees. Sapwood occupied the outer 1–2 cm of wood in younger, smaller trees and 2–3 cm in older, larger trees (Fig. 1A and B). Younger trees with wide outer decadal bands tended to have a single band of actively conducting sapwood while older trees with narrow outer bands tended to have two or more decadal bands of sapwood (Fig. 1C).

3.2. Decadal trends of Ca, Mg, and K in northeastern red spruce

For the northeastern red spruce collection as a whole, decadal concentration of K was stable across the heartwood of the 1860s through the 1940s, at about one-half the concentration of the outermost decadal band of sapwood (Fig. 3A). The outer 4 decadal bands, 1950s–1980s, progressively increased in mean K concentration with the greatest interdecadal increase for the 1970s (Fig. 3B). Mean Ca concentration of heartwood bands decreased from the tree center outward (Fig. 3C) reaching a plateau for the 1940s–1960s followed by significant decreases in the 1970s and 1980s of about 3.5% per decade (Fig. 3C and D). The mean concentration of Mg followed the same pattern as Ca until the 1960s with the significant 4% interdecadal increase of Mg in the inner sapwood (Fig. 3E and F). In the outermost sapwood band of the 1990s, the interdecadal concentration of Mg significantly decreased by 8%.

3.3. Effects of tree age and size

The outermost 2 cm of wood in both the younger and older cohorts of northeastern red spruce collected in the early 1990s contained the decadal bands formed in the 1970s and 1980s and conducting sap (Fig. 4A, solid and dashed lines). If the same two cohorts were sampled in the early 1970s, the tree-ring record indicated that both decadal bands of the older cohort would be conducting sap in outer two bands formed in the 1950s and 1960s (Fig. 4B, solid line). However, the younger cohort would only be conducting sap in the outer decadal band formed in the 1960s because the 1950s band would have become non-conducting heartwood (Fig. 4B, dashed line).

In older slower growing trees, interdecadal changes in Ca concentration significantly increased in the 1950s and significantly decreased in the 1970s and 1980 (Fig. 4C). In the younger, faster growing trees the interdecadal change in Ca was generally negative but with a significant increase in the 1960s and significant decreases in the 1970s and 1980s (Fig. 4 D).

Although interdecadal changes in Mg concentration (Fig. 4E and F) were similar to those for Ca (Fig. 4C and D), there were some difference in the outer three decadal bands. In older trees, the inner heartwood contained negative interdecadal changes in Mg concentration and the outermost sapwood band contained a significant decrease. Younger trees had significantly negative interdecadal changes in Mg concentration with a single positive band for the 1960s. Red spruce had significantly positive interdecadal change of K concentration for the outer 4 or 3 decadal bands in older and younger trees, respectively (Fig. 4G and H). The single increase in Mg was coincident with a significant increase in interdecadal K concentration in the 1960s with a sustained high level of K in the outermost four decadal bands of the older trees (Fig. 4G).

3.4. Position of peak interdecadal change

Grouping dendrochemical series by the interdecadal band of peak change in Ca concentration obtained patterns of significant peak increases in concentration. For the red spruce sampled in 1992–1994, the greatest frequency of occurrence for maximum

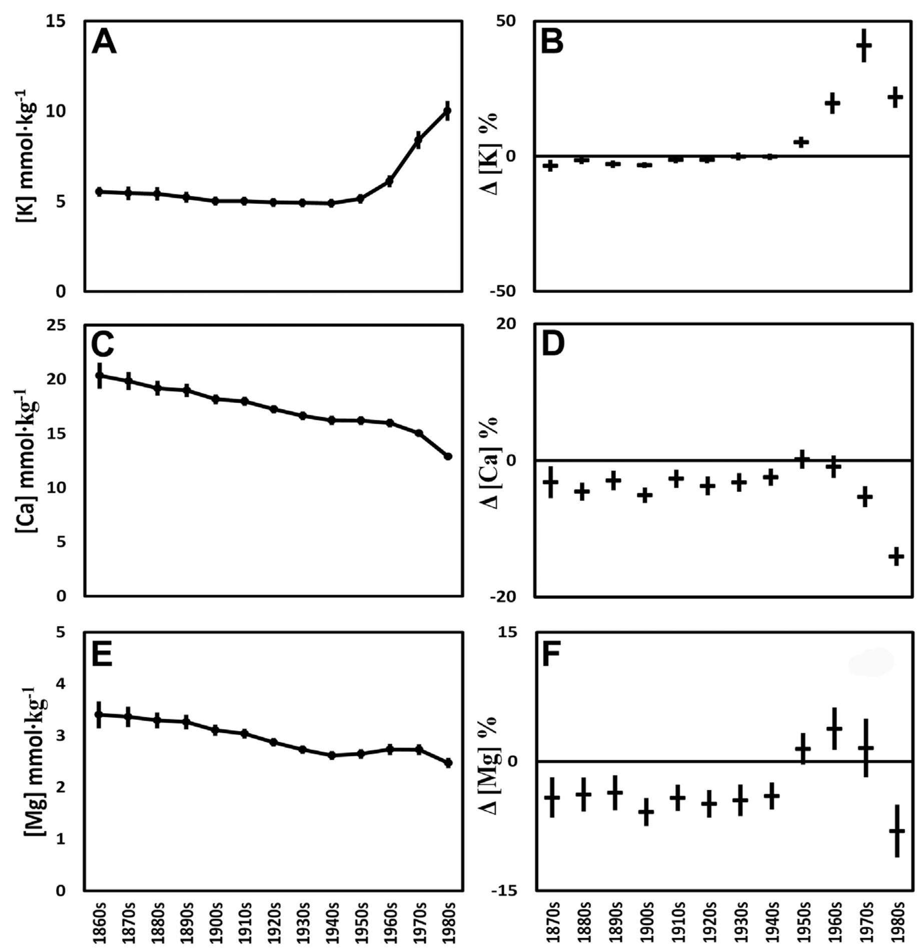

Fig. 3. Summary trends in cation concentration for northeastern red spruce. (A, C, E) Mean concentrations and 95% confidence intervals of K, Ca, and Mg of decadal bands from 1860s to 1980s (n = 36 to 104 trees/decade from 1860s to 1900s, n = 123 trees/decade from 1910s to 1980s). (B, D, F) Mean interdecadal change in concentration and 95% confidence intervals (CI) for K, Ca, and Mg. Significantly positive and negative interdecadal change are indicated by CI wholly above or below the horizontal "0" line, respectively. No significant interdecadal change is indicated by CI that intersect the "0" line.

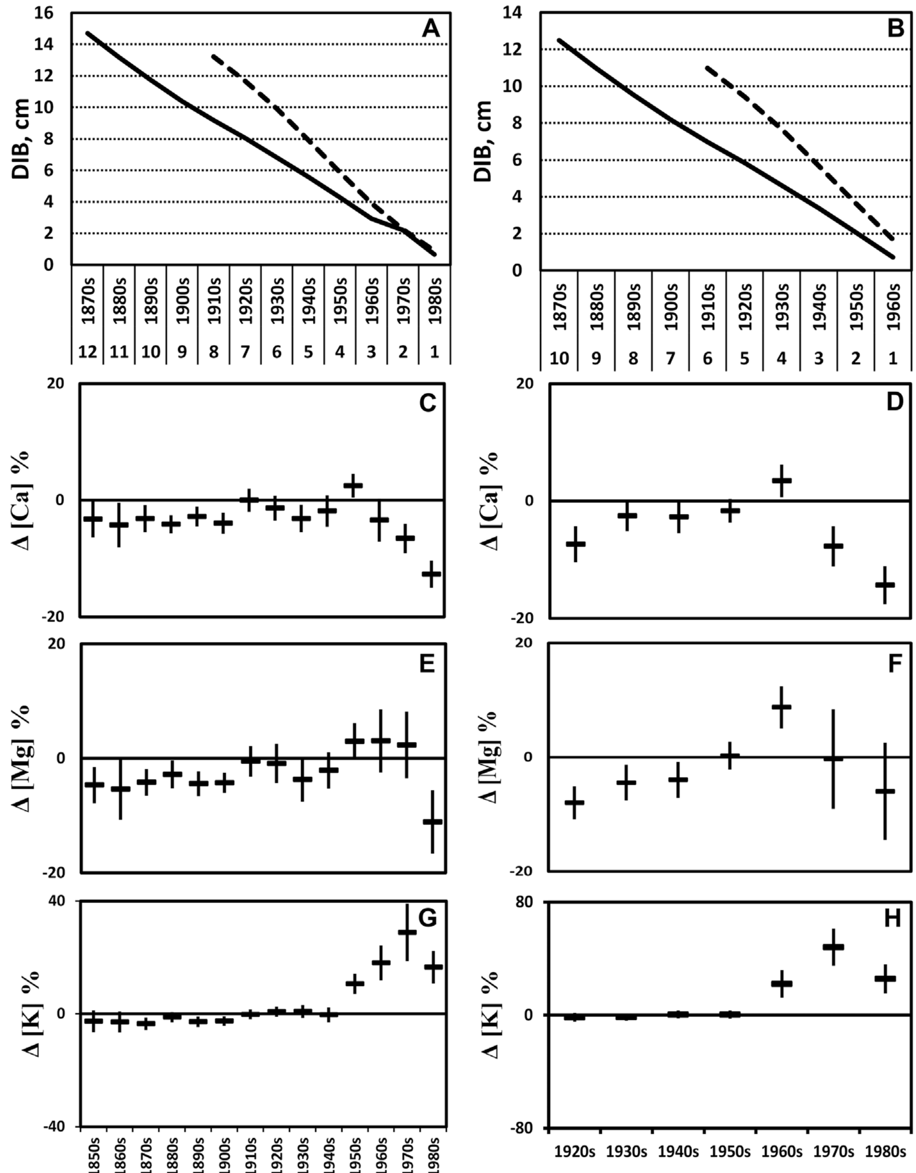

Fig. 4. Observed and modelled effect of ring width on cation concentration for northeastern red spruce. (A) Relationship of decadal bands to radial distance inside bark (DIB) of older (solid line) and younger (dashed line) northern red spruce sampled in 1992–1994. (B) Estimated distance inside bark for decadal bands in these trees if sampled in the early 1970s. (C–H) Mean interdecadal change of cation concentration in trees with narrow (C, E, G) or wide (D, F, H) interdecadal spacing for Ca (C, D), Mg (E, F), and K (G, H). Significant differences ($P \le 0.05$) for the interdecadal change in concentration are the same as in Fig. 2.

interdecadal change in Ca was the 1950s band (33%). For the red spruce resample of 2002–2004, the greatest frequency of occurrence was for the 1970s band (44%, Table 1). When all series within a group were pooled, irrespective of the position of peak interdecadal change in Ca concentration, no significant increase in Ca was observed in any decade for both the initial northeastern red spruce collection and for the resample collection (Table 1).

The percentage of trees with a positive interdecadal change for Ca in the 1960s was similar for the initial northeastern red spruce and the resample (30% and 28%, respectively.) For those series, subsequent interdecadal changes in Ca were consistently and significantly negative (Table 1). The percentage of trees with a positive interdecadal change of Ca in the 1970s increased from 14% to 44% for the initial collection and resample, respectively. The percentage of trees without a positive increase in the 1950s, 1960s, or 1970s decreased from 14% to 4%.

Interdecadal increases in Mg were evaluated for trees grouped by the decade of maximum interedecadal concentration of Ca (Table 2). This grouping aided comparison of Ca and Mg dynamics within the same sets of trees. When all series were pooled within collections, the 1960s band contained a significantly positive interdecadal change in Mg for both the initial collection and for the resample.

3.5. Southern Appalachian red spruce

For southeastern red spruce (Fig. 5A), the mean trend of interdecadal change of Ca concentration included a significant increase for the 1950s band, the same as the comparable set of northeastern spruce. The 1970s and 1980s band of southern spruce contained significant decreases in interdecadal changes in Ca concentration. The 1920s decadal band in the southern spruce also contained a

Table 1
Mean interdecadal change in Ca concentration in northeastern red spruce sampled in 1992–1994 and resampled in 2003–2004.

Decade of maximum Ca increase[a]	n	%	Mean interdecadal change in Ca concentration (%)[b]					
			1940s	1950s	1960s	1970s	1980s	1990s
			Decadal bands sampled in 1992–1994					
1940s	16	13	**+8.5** *	−5.4 *	−6.1 *	−7.6 *	−13.8 *	
1950s	40	33	−3.7 *	**+8.1** *	−4.8 *	−4.9 *	−15.4 *	
1960s	34	28	−2.9 *	−2.4 *	**+8.5** *	−9.8 *	−14.5 *	
1970s	17	14	−4.8 *	−3.3 *	−3.2	**+5.5** *	−11.4 *	
None	16	13	−6.8 *	−4.9 *	−3.4 *	−5.9 *	−12.8 *	
All	123	100	−2.4 *	+0.2	−0.9	−5.3 *	−14.0 *	
			Decadal bands resampled in 2003–2004					
1940s	2	7						
1950s	4	15	−7.8	+10.7	−7.3	−3.5	13.4 *	−6.6 *
1960s	8	30	−4.3	−4.0	**+13.3** *	−6.4	−5.5	−8.0 *
1970s	12	44	−5.7 *	−3.2	−1.7	**+6.9** *	−10.8 *	−6.5 *
None	1	4						
All	27	100	−4.0 *	−1.4	+1.7	+0.3	−9.3 *	−6.3*

[a] Trees were grouped by the decade of maximum significant interdecadal increase in Ca. The "None" group contains trees with no significant increases in interdecadal Ca concentration. Values for the complete set of all northeastern spruce is marked "All".
[b] Maximum interdecadal increase in Ca is given in bold type. Statistical significance ($P \leq 0.05$) is indicated by *.

Table 2
Mean interdecadal change in Mg concentration in northeastern red spruce sampled in 1992–1994 and resampled in 2003–2004.

Decade of maximum Ca increase[a]	n	%	Mean interdecadal change in Mg concentration (%)[b]					
			1940s	1950s	1960s	1970s	1980s	1990s
			Decadal bands sampled in 1992–1994					
1940s	16	13	**+5.5** *	−5.9	−0.5	−5.0	−4.1	
1950s	40	33	−6.8 *	**+9.2** *	−0.6	+3.9	−10.4 *	
1960s	34	28	−3.4 *	−1.1	**+12.0** *	−5.5	−7.0	
1970s	17	14	−6.5 *	−1.9	+3.4	+8.5	−9.0 *	
None	16	13	−5.2 *	−1.4	+2.1	+9.8	−7.6 *	
All	123	100	−4.0 *	+1.5	+3.8 *	−5.3 *	−8.1 *	
			Decadal bands resampled in 2003–2004					
1940s	2	7						
1950s	4	15	−12.1	+4.9	0.0	+3.2	−6.3	−13.9 *
1960s	8	30	−6.1	−3.4	**+15.9** *	−5.1	−2.3	−0.2
1970s	12	44	4.7 *	−1.2	+2.5	**+9.2** *	−9.3 *	−3.6 *
None	1	4						
All	27	100	+5.1 *	−0.8	**+6.5** *	+4.8	−6.6 *	−4.3

[a] Trees were grouped by the decade of maximum significant interdecadal increase in Ca as in Table 1. The "None" group contains trees with no significant increases in interdecadal Ca concentration. Values for the complete set of all northeastern spruce is marked "All".
[b] Maximum interdecadal increase in Mg is given in bold type. Statistical significance ($P \leq 0.05$) is indicated by *.

significant increase in Ca concentration (Fig. 5A) which was not evident in the comparable northeastern spruce trend.

In both the northeastern and southern red spruce collection, the interdecadal increase in Ca in the 1950s was followed by decreases in the 1970s and 1980s (Fig. 5A). In the southern red spruce, an interdecadal increase in Ca occurred in the 1920s (Fig. 5A) and concentrations remained high for the southern compared to the northern spruce through 1980s (Fig. 5C). Wood Mg was greater in the south than the north over the entire life of the trees (Fig. 5D) and no significant interdecadal changes in Mg occurred in the 1940s through the 1980s (Fig. 5B). The pattern of K concentration of both northern and southern population were virtually identical (Fig. 5E).

3.6. Soil calcium and dendrochemistry of Norway spruce in northwestern Russia

Analytical comparisons of recently collected and archived soil samples show marked declines in concentration of exchangeable Ca and an increased molar proportion of Al/Ca for both the 0–10 and the 10–20 cm sampling depths (Fig. 6A and B).

About 40% of the tree cores taken had visual symptoms of decay, likely caused by a common root and butt rot disease of Norway spruce. Of the remaining 21 asymptomatic cores, 13 were from healthy trees in which K was resorbed (resorption index < 1) as sapwood matured to become heartwood and Ca and Mg were retained (resorption index ≥1) (Fig. 6 healthy). The other 8 were from diseased trees in which K concentrations of inner bands exceeded those of outer sapwood concentrations indicating the spread of wound-initiated infection (Fig. 6 diseased). There is also a marked increase in the resorption index of Mg in the inner bands of heartwood of Norway spruce.

Pooled series consisting of both healthy and diseased trees yielded no significant interdecadal increase in Ca or Mg (Fig. 6C and D). However when separated, a significant interdecadal increase occurred in for the 1940s (Fig. 6E), coincident to the period of Ca depletion between 1926 and 1964 (Fig. 6A). No further change occurred in the 1950s band followed by significant decreases in the 1960s and 1990s band. The interdecadal changes of Mg followed the same patterns as Ca, except that there was no significant decrease in the outermost sapwood band of the 1990s (Fig. 6 F).

4. Discussion

The dendrochemical record in US red spruce and Russian Norway spruce is consistent with the context of cation mobilization,

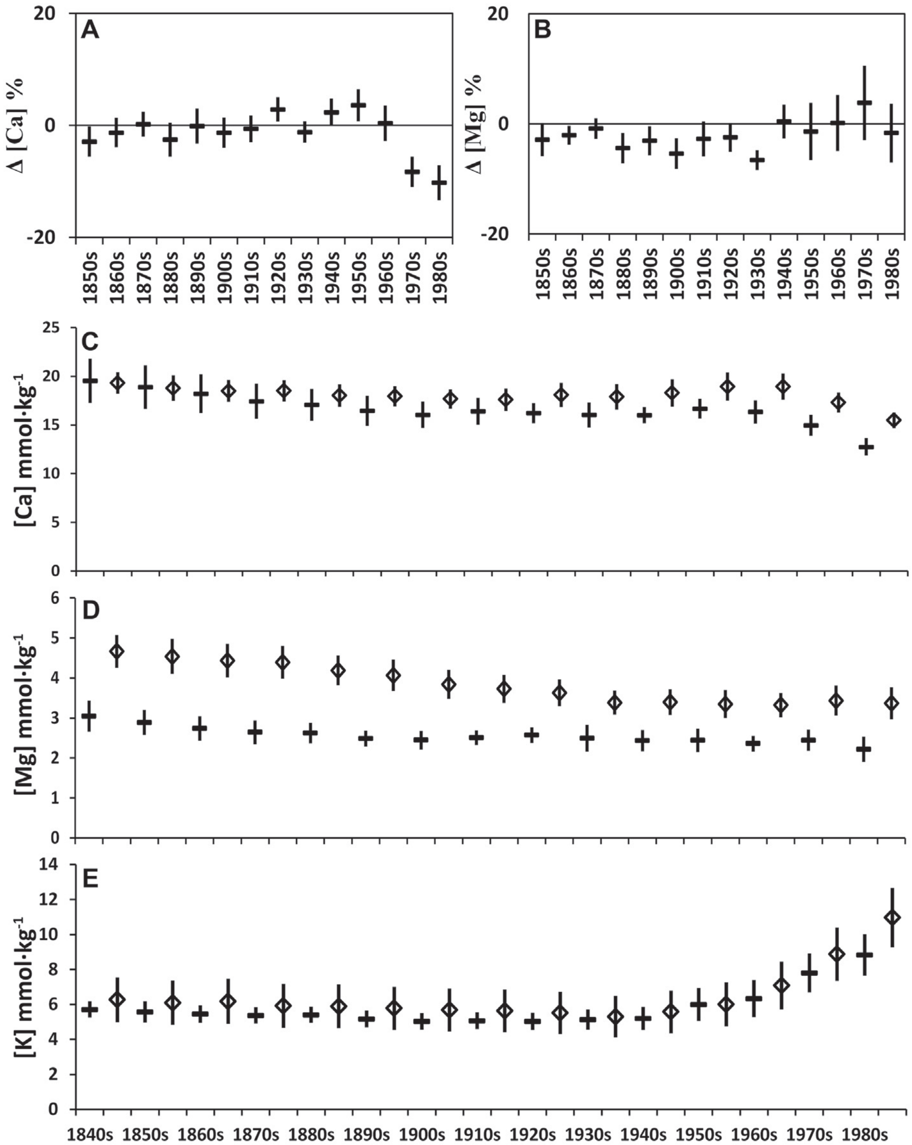

Fig. 5. (A, B) Means and 95% confidence intervals of interdecadal change in Ca and Mg concentration for 17 older red spruce in the southeastern US (C, D, E). Means and 95% confidence intervals of Ca, Mg and K concentration of decadal bands of these southeastern trees (diamonds) compared to 13 trees of similar age and stature in the northeastern US (dashes). Lack of overlapping CI indicates significant differences ($P \leq 0.05$).

depletion, and recovery described for those forests (Lawrence et al., 2015). Peak increases in deposition of strong acid anions in the 1970s was recorded as significant increases in mobilized Ca for the decadal bands of the 1950s and 1960s. Initial recovery following reduced emissions in the 1990s and cycling fueled by decaying wood was recorded as significant increases in Ca for the 1970s decadal band. Significant interdecadal increases in Ca concentration are especially noteworthy as the ion-exchange binding capacity tends to decrease with increased radial distance from the center of the stem (Momoshima and Bondietti, 1990). The identification and interpretation of the record of environmental change in individual tree-ring series was complicated by previously identified internal processes of maturation and presumptive infection. Construction of site or regional dendrochemical series are further complicated by age and other differences among trees.

Although the root uptake of base cations from the soil is to some degree selective, uptake would likely be affected by environmental conditions that affect soil moisture and transpiration on an individual-tree and landscape basis. As used here, the decadal approach for sampling, chemical analysis, and data presentation reduces the influence of extremes in annual weather patterns. Cyclic or quasi-periodic environmental factors such as the North Atlantic Oscillation may have an effect on decadal dendrochemical patterns, through influences on radial growth and indirectly on sapwood width. Such potential effects are beyond the scope of this report.

In the process of heartwood formation from sapwood, K is retained by the sapwood symplast and is removed or resorbed from older rings (Meerts, 2002). Significant interdecadal increases in K for spruce heartwood were interpreted as a marker of infection by microorganisms based on extensive previous research on the chemistry of infected wood in living trees (e.g., Shortle and Smith, 1987).

In spruce, Ca translocation is apoplastic and not resorbed. Translocated in both apoplast and symplast, Mg was resorbed by the sapwood symplast. Consequently, sapwood width played a

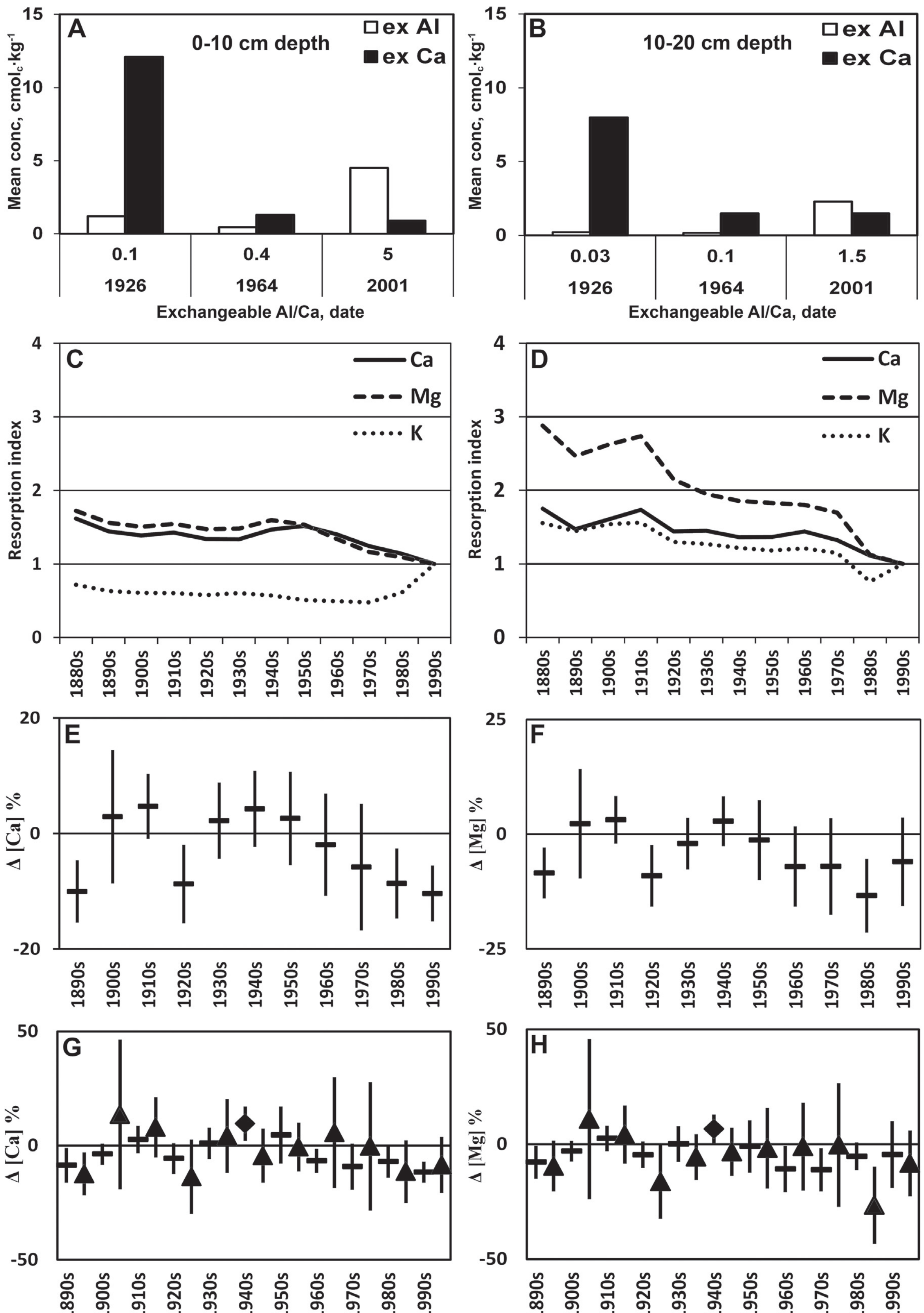

Fig. 6. Mean concentration of exchangeable Ca and Al of mineral soil at depths of 0–10 cm (A) and 10–20 cm (B) from repeated sampling of a Norway spruce forest in northeastern Russia. (C, D) Resorption index for healthy (n = 13) and diseased (n = 8) Norway spruce, respectively. Means and 95% confidence intervals of interdecadal change in Ca and Mg when healthy and diseased tree were combined (E, F respectively, n = 21) or separated (G, H respectively). Separated means for healthy and diseased trees are marked as bars and triangles, respectively. The 1940s interdecadal mean for healthy trees was significantly greater for both Ca and Mg (diamond).

crucial role in the spruce dendrochemical record. Translocation within sapwood is not uniform with inner sapwood being less conductive than outer sapwood (Spicer and Gartner, 2001). Active sapwood has the potential to be exposed to pulses of cation availability, while non-conducting heartwood is not available to record such a pulse. This fundamental property of wood function has as great a bearing on dendrochemical patterns as the more frequently questioned stability of concentration in specific rings over time. We expect that this role of sapwood width in cation concentration to be especially relevant for cations such as Ca with a structural function within the wood matrix.

Given that a rapid increase in acidic deposition in the 1960s mobilized exchangeable Ca (Shortle et al., 1997) to yield Ca-enriched sap, the expected enrichment of sap-conducting sapwood immediately beyond non-conducting heartwood would occur in the first (1960s), second (1950s), or third (1940s) decadal band of sapwood depending on the number of decades of sapwood present. Fast growing trees with wide annual rings contained only a single decadal band of sapwood formed in the 1960s. Slow growing trees with narrow rings contained three bands of sapwood. Consequently, the greatest increase in Ca would occur in the 1940s decadal band, which was the innermost sap-conducting decadal band. When cores were grouped by the decade of maximum interdecadal increase in Ca concentration (Table 1), the two most common patterns accounting for 61% of the sample cores taken at the beginning of the 1990s were the 1950s, which represents the inner band of a tree with two outer bands actively conducting sap, and the 1960s, which represents trees with a single band of actively conducting sap.

The cation mobilization which at first resulted in Ca enrichment soon resulted in Ca depletion and a significant negative interdecadal change. Given the approximately equally frequency of occurrence of trees with maxima in the decades of 1950s and 1960s, the negative temporal changes cancel out the positive changes when decadal bands of trees with substantially different rates of incremental growth (and therefore differences in the number of sap-conducting decadal bands) were averaged together. Combining results of cores from trees of different age groups, growth rates, associated sapwood width masks trends in wood chemistry from which to infer changes in the availability of essential mineral elements. This limits the efficacy of dendrochemical investigations to study ecological processes such as the response and recovery of soil conditions to acid rain.

Three additional patterns were observed for the remaining 39% of the red spruce series. The first pattern (13%) was for trees which had three decadal bands of sapwood with a significant increase in the 1940s decadal band. The second pattern (12%) showed no significant interdecadal increases, only decreases in Ca concentration. The third pattern (14%) showed a significant interdecadal increase in the 1970s.

After one decade of recovery through (1) reduced emissions of acid-forming gases and subsequent deposition and (2) increased wood decay on and in the forest floor and from decaying woody roots, the frequency of positive interdecadal changes in the 1970s for the northeastern red spruce resample increased three-fold from 14% to 44%. The frequency of trees with only negative changes decreased from 13% to 4%, a threefold decrease. The frequency of trees with a significant positive interdecadal increase in the 1960s remained about the same, and those with prior positive changes decreased as the older larger trees in which such changes were common have continued to die and decay and are no longer available to sample. Although the interdecadal increase in Ca was greatest for the 1950s in some trees, there were too few for statistical significance. For the resampled spruce, the greatest interdecadal increase of Ca was for the 1970s (Table 1). This increase is consistent with the 1970s band conducting sap during the period of improved availability of Ca for root uptake described on the basis of improving soil and water chemistry (Lawrence et al., 2015).

Interpretation of decadal dendrochemical series of Russian Norway spruce required sorting to remove series affected by early stages of infection. After sorting, a significant interdecadal increase was followed by a decadal band with a sustained high concentration. Later bands contained significant decreases in interdecadal changes. We interpret this as two bands of sapwood conducting at the time of cation mobilization, followed by cation depletion as evidenced by the comparative soil analysis of archived and more recently collected forest soil.

For both US red spruce and Russian Norway spruce, interdecadal changes for Mg were similar to Ca except that significant negative interdecadal changes did not follow the positive changes in the case of Ca. We interpret this pattern as due to the active resorption of Mg along with K as the sapwood symplast was withdrawn during heartwood formation. The pattern of temporal change in dated wood for Ca was produced by wall-bound Ca, but the temporal change for Mg involved both the wall-bound portion as for Ca and the cell-bound portion as K. This resulted in a strong positive interdecadal increase in the 1960s during maximum acid input. After one decade the maximum increase in the 1960s was retained and the increase in the 1970s further indicated a period of Ca and Mg enrichment following the period of Ca depletion in root-zone soil.

The results to-date indicate two sources of increased Ca in the wood record of northeastern red spruce. The first is cation mobilization by increased acid input in the 1960s. The introduction of strong acid anions displaced exchangeable Ca and Mg from storage sites in root-zone soil. Cation mobilization provided a relatively brief period of availability for root uptake and transfer to cation exchange sites in wood cell walls. The second source of increased Ca was biogeochemical cycling including tree death and decay that had begun to enrich root zone soil with exchangeable Ca (Shortle et al., 2012). This replenishment of exchangeable base cations in the 1990s was recorded as a significant interdecadal increase in sapwood formed in the 1970s.

A third cause of increased Ca in dated wood occurred in the southern population of red spruce in which a significant positive interdecadal change was observed in the 1920s. We suggest that deposition of Ca-rich dust during the Dust-Bowl period of the 1930s enriched forest soils in the southeastern US. Published accounts indicated large amounts of air-borne particulates reached the eastern seaboard in the 1930s (Simonson, 1995; Watson, 1934). This decade of enrichment by atmospheric base deposition was not followed by a significant negative interdecadal change as in the case of base mobilization as occurred in the 1950s. The Ca concentration of all decades from the 1840s to the 1920s did not differ significantly between the two regions, but after the 1930s the southern population differed significantly until the 1980s indicating a long-term effect of base deposition on Ca uptake.

The major challenge of using the elemental chemistry of dated wood in mature trees to determine external temporal changes in root-zone soil is separating internal changes associated with maturation of the trees from pith to bark, maturation of the wood from bark to pith, and the development of columns of wound-initiated decay. Chemical changes in wood prior to visible symptoms of wood decay are detectable as changes in K concentration, relative to the outermost sapwood. Red spruce and Norway spruce did not resorb Ca and Mg as sapwood matured.

Calcium was recognized as a key component of forest productivity early in the 20th century (Perry, 1928). In the CO_2-enriched atmosphere of the early 21st century, inadequate soil fertility can limit forest growth and C sequestration (Oren et al., 2001).

Although forest growth is often primarily related to N availability, limited Ca can shift C allocation from production of stemwood with a long residence time to fine roots that are rapidly shed and decomposed (Lapenis et al., 2013). Reduced acidic deposition has begun to improve soil conditions for tree growth (Lawrence et al., 2012, 2015). Continuing that improvement requires microbiological processes including the restoration of root-available Ca to root-zone soil by the action of wood-decay fungi and the sustained supply of N and P by the action of ectomycorrhizal fungi (Shortle and Smith, 2015). Studying patterns of temporal change in dated wood at the decadal scale provides a method to infer periods of depletion and restoration of essential elements that are part of the biogeochemical cycling taking place in forests for which long-term soil sampling and analysis is lacking.

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