

# Ecosystem Processes

## Spatial Variations of Sapwood Chemistry with Soil Acidity in Appalachian Forests

David R. DeWalle,\* Bryan R. Swistock, Roger G. Sayre, and William E. Sharpe

### ABSTRACT

Studies were conducted at five Appalachian sites to determine if chemical element concentrations in sapwood tree rings from six tree species varied with soil and soil leachate acidity. The most recent 5-yr-growth increment was extracted from 10 tree boles of each species at each site and analyzed for chemical content using plasma emission spectroscopy. Sapwood tree rings generally showed higher concentrations of Mn and lower concentrations of Sr at sites with lower soil pH. Differences in tree-ring concentrations for Ca and Mn among sites were also found in soil water samples at these sites. Significant differences in soil leachate Al between sites were not duplicated in tree rings. Sapwood tree-ring chemistry in red oak (*Quercus rubra* L.), black cherry (*Prunus serotina* Ehrh.), eastern white pine (*Pinus strobus* L.) and eastern hemlock (*Tsuga canadensis* [L.] Carr.) was generally responsive to differences in soil chemistry between sites. Chestnut oak (*Q. prinus* L.) and pignut hickory (*Carya glabra* [Mill.] Sweet) were the least responsive species tested. Overall, results show that several common tree species and selected elements are potentially useful for studying historic soil acidification trends at these study sites.

ONE POTENTIAL METHOD for determining historic time trends of soil acidification is analysis of trends in tree-ring chemistry. Gradual acidification of soils due to atmospheric deposition and natural processes could increase solubility and availability of metals such as Mn and Al. Soil acidification could also be accompanied by declines in availability of base cations such as Ca, Mg and related alkali and alkaline earth metals. Alternatively, increases of mobile SO<sub>4</sub> anions

in soil solution from atmospheric deposition could increase mobility and availability of base cations in soil leachate. Regardless, soil acidification should be accompanied by several changes in soil element availability for uptake and storage in tree rings.

Patterns in tree-ring chemistry have been used to infer changes in the soil chemical environment. Bondietti et al. (1989) showed that Al/Ca ratios in increment cores from red spruce (*Picea rubens* Sarg.) in Tennessee and North Carolina increased during the past 15 to 40 yr. This study also provided circumstantial evidence that increases in soil Al mobilization were due to atmospheric deposition of SO<sub>4</sub> and NO<sub>3</sub> and that Al mobilization was possibly the cause of reduced red spruce radial growth in the past 30 yr. In a similar study, Guyette et al. (1989) used Mo concentrations in Missouri eastern redcedar trees (*Juniperus virginiana* L.) to infer that increasing heartwood S since 1860 was due to increasing soil SO<sub>4</sub> concentrations from atmospheric deposition. Other recent studies have correlated soil chemistry with xylem concentrations of tree rings in several deciduous and coniferous tree species (Legge et al., 1984; Frelich et al., 1989; McClenahan et al., 1989).

Despite the impressive results of these studies in linking tree-ring chemical patterns to variations in soil chemistry, the use of tree rings as indicators of historical conditions has several limitations. Possible problems include translocation and redistribution of elements, variation in mechanisms of element uptake, uncertainty of relationships between tree-ring uptake and environmental concentration of pollutants and variability among tree species (Lepp, 1975; McClenahan et al., 1989).

Past studies indicate that translocation or lateral movement of elements after wood formation is the most prevalent problem associated with the use of

D.R. DeWalle, B.R. Swistock, W.E. Sharpe, School of Forest Resources, Pennsylvania State University, University Park, PA; 16802; and R.G. Sayre, 110 Ridgecrest Rd., Ithaca, NY, 14850. Received 23 Sept. 1989. \*Corresponding author.

Published in J. Environ. Qual. 20:486-491 (1991).

tree-ring chemistry. McClenahen et al. (1989) found that only Fe, Si, Al, Cu and Sr of 14 measured elements were considered immobile in tulip-poplar xylem (*Liriodendron tulipifera* L.). Baes (1985) suggested that Mg, Ca, Sr, Mn and Zn in conifers may be translocated from younger to older tree rings. Other researchers have demonstrated lateral mobility of Zn, Cd, Cu and Pb in various tree species (Barnes et al., 1976; Symeonides, 1979; Baes and Ragsdale, 1981).

The mechanism which conveys an element to the wood tissue must be understood to relate wood chemistry patterns to changes in environmental pollutant concentrations. Elements can be incorporated into wood not only through root uptake from soil solutions but also via atmospheric deposition and absorption through bark and leaves. Lepp (1975) provides a summary of these pathways of element uptake with regard to heavy metals. Because atmospheric inputs are a major source of trace and heavy metals, several researchers have used these elements to study air pollutant histories (Baes and Ragsdale, 1981; Baes and McLaughlin, 1984; Legge et al., 1984; Maclauchlan et al., 1987). Other studies which were interested in historical variations in soil chemistry have primarily utilized alkaline earth metals such as Be, Mg, Ca, and Sr (Bondietti et al., 1989; Frelich et al., 1989; McClenahen et al., 1989; Long and Davis, 1989).

Due to physiological or site characteristics, the response of various tree species to changes in soil chemistry could vary significantly. Obviously, comparisons cannot be made across species but selection of species which are sensitive to changes in atmospheric deposition or the soil chemical environment are necessary. For example, McClenahen et al. (1989) found that tulip trees could not be used to identify historical deposition or soil chemical changes at a particular site due to translocation and inherent chemical differences between heartwood and sapwood. However, others have shown that eastern redcedar, white pine, sugar maple (*Acer saccharum* Marsh.), red spruce and eastern hemlock are sensitive to soil chemical changes (Bondietti et al., 1989; Frelich et al., 1989; Guyette et al., 1989).

As a preliminary step towards the use of tree-ring chemistry to detect soil acidification in the Appalachians, this study was conducted to determine which soil-associated elements and which common Appalachian tree species were responsive to variations in soil

and soil leachate acidity among several forest sites. If elements and tree species which respond to variations in soil and soil leachate acidity can be identified, then chronologies of tree-ring chemistry for specific elements and species could be examined for potential soil acidification.

## METHODS

### Field Sampling

Tree-ring and soil data were collected for five Appalachian forest sites (Table 1). All trees sampled were dominant or codominant trees without obvious major trunk or canopy defects. Tree-ring cores were extracted at breast height using increment borers coated with Teflon which were rinsed with acetone and deionized water prior to each extraction. Cores were also rinsed with deionized water after extraction and after preparation for shipment for chemical analysis. Clean plastic gloves and scalpels were used when handling cores. Lengths of all core segments were measured.

Five-year-growth increments in 10 trees of each of two species were sampled in fall 1984 at three sites. Red oak and chestnut oak trees were sampled at Fork Mountain, WV, Pea Vine Hill, PA, and Sand Mountain, PA. The Fork Mountain site generally exhibited significantly higher soil pH than the Pea Vine Hill and Sand Mountain sites (Table 1). Black cherry trees were not found at Sand Mountain and, thus, were only sampled at Fork Mountain and Pea Vine Hill. One 12-mm-diam. core was extracted from each of the 10 trees at each study site.

Three other common Appalachian tree species, white pine, Eastern hemlock and pignut hickory, were compared at the Rockview, PA and Alan Seeger, PA sites. Soils at Rockview were derived from dolomite bedrock resulting in a higher soil pH than the Alan Seeger site (Table 1). Ten trees of each species were also sampled at each of these two sites. Eight, 4-mm-diam. cores were extracted from each tree in winter-spring 1986 and composited to obtain enough mass for analysis and to reduce circumferential variability. Again, only the most recent 5-yr-growth increment was used in analysis. Additional details on this study were reported by Sayre (1987).

Soil and soil leachate chemistry data were available from other studies to aid in interpreting tree-ring chemistry (DeWalle and Sharpe, 1985; DeWalle et al., 1988; Sayre, 1987). Triplicate soil samples from each rooting zone soil horizon were collected from soil pits at each site. Soil leachate samples were collected with zero-tension and tension ceramic-cup lysimeters at all sites except Rockview and Alan Seeger.

Table 1. Description of the locations, soils, geology, and tree species sampled at the study sites.

Site	Fork Mountain	Pea Vine Hill	Sand Mountain	Rockview	Alan Seeger
State	WV	PA	PA	PA	PA
Latitude/longitude	39°03'N/ 79°41'W	40°10'N/ 79°09'W	40°45'N/ 77°95'W	40°51'N/ 77°79'W	40°41'N/ 77°46'W
Species sampled					
Red oak ( <i>Quercus rubra</i> L.)	X	X	X		
Chestnut oak ( <i>Q. prinus</i> L.)	X	X	X		
Black cherry ( <i>Prunus serotina</i> Ehrh.)	X	X			
Eastern white pine ( <i>Pinus strobus</i> L.)				X	X
Eastern hemlock ( <i>Tsuga canadensis</i> [L.] Carr.)				X	X
Pignut hickory ( <i>Carya glabra</i> [Mill.] Sweet)				X	X
Soil Series	Dekalb/Berks	Hazleton/Leckkill	Hazleton	Opequon	Buchanan/Berks
pH (A and/or E horizons)	4.77-4.92	3.49-4.24	3.80	5.55	4.6
Bedrock geology					
Type	Sandstone/Shale	Sandstone/Shale	Sandstone	Dolomite	Shale
Formation	Hampshire	Mauch Chunk	Juniata	Nittany	Clinton

† Cited from DeWalle and Sharpe (1985), and Sayre (1987).

**Laboratory Analysis**

Laboratory analyses were identical for both studies. Woodcores were oven dried, weighed, ashed, and digested in 20% nitric acid prior to analysis (Jones, 1977). Cores were analyzed for P, K, Ca, Mg, Fe, Mn, B, Cu, Zn, Na, Al, Si, Co, Cr, Ni, Pb, Cd, Sr, Ba, and Be at the Institute of Ecology, University of Georgia with a Jarrel-Ash inductively coupled plasma emission spectrometer (ICP) (Thermo Jarrell Ash Inc., Waltham, MA). Calibration of the ICP was based on Standard Reference Materials 1571 (citrus leaves), 1575 (pine needles), and 1577a (bovine liver) available from the National Institute of Standards and Technology, Standard Reference Materials Program, Bldg. 202, Room 204, Gaithersburg, MD 20899. Solution standards were prepared from ICP single element (1000 ppm) standards and referenced to the Standard Reference Materials listed above. The ICP was calibrated using the prepared solution standards and the standards were later rerun as "unknowns" to verify calibration.

Because the objective of this study was to relate tree-ring chemistry to soil chemical conditions, comparisons were limited to those elements which would likely reach the wood tissue via root uptake (i.e. soil source). Thus, elements discussed in this paper are limited to Ca, Mg, Mn, Na, Al, Si, Sr, Ba and Be. Duplicate pair analyses from wood cores split longitudinally indicated median differences of less than 5% for Ca, Mg, Mn, Na, Sr and Be. Median values of split sample analyses for Al ranged between 10 and 30%. Comparisons of median tree-ring chemical element concentrations among

sites in both studies were performed using Tukey's nonparametric comparison (Neter et al., 1985) at an  $\alpha = 0.05$ .

Soil samples were analyzed for pH at the Merkle Soil Characterization Laboratory on the Pennsylvania State University campus. Soil pH was measured on a 1:1 soil-distilled water mixture. Soil leachate analysis was performed at the Environmental Resources Research Institute, also on the Pennsylvania State University campus, using U.S. EPA recommended procedures (Environmental Protection Agency, 1983, 1984).

**RESULTS AND DISCUSSION**

Data from the first study were analyzed to compare three tree species (red oak, chestnut oak, black cherry) among three sites with varying soil chemistry (Fork Mountain = least acidic; Sand Mountain = moderately acidic; Pea Vine Hill = most acidic). Median chemical element concentrations in the most recent 5-yr-growth increment varied significantly with soil acidity among forest sites, but the differences were highly species and element specific. Comparisons of red oak tree-ring chemistry among the three sites show that concentrations of Ca, Sr and Be were significantly higher and concentrations of Mn were significantly lower at Fork Mountain than at the more acidic Pea Vine Hill and Sand Mountain sites (Fig. 1). Red oak data for Na, Si and Al were not significantly different

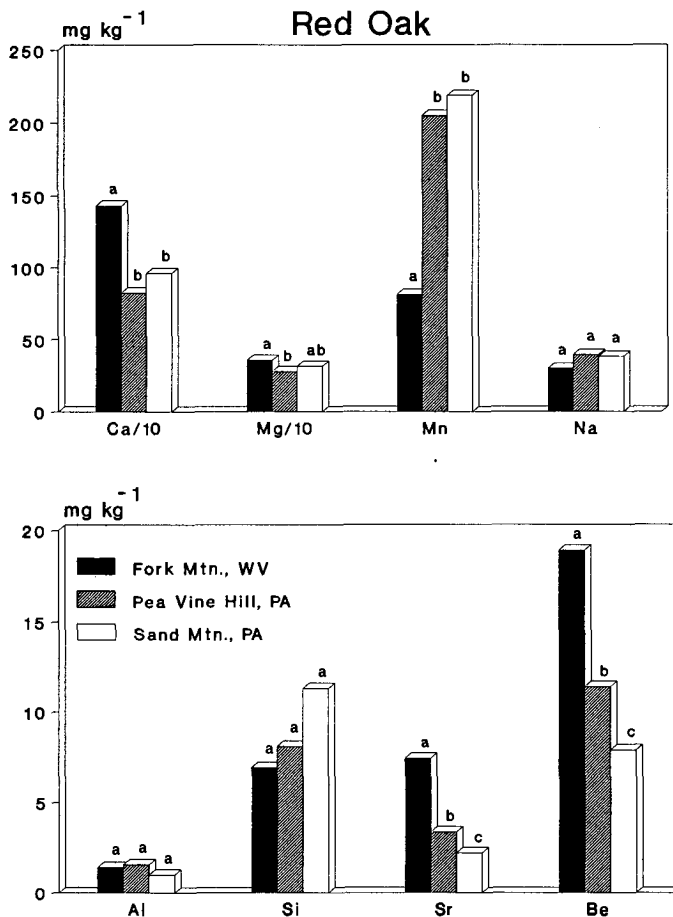


Fig. 1. Median chemical element concentrations of recent tree rings (1980-1984) in red oak (*Quercus rubra* L.) at three sites. Different letters above bars indicate medians are significantly different at  $\alpha = 0.05$ .

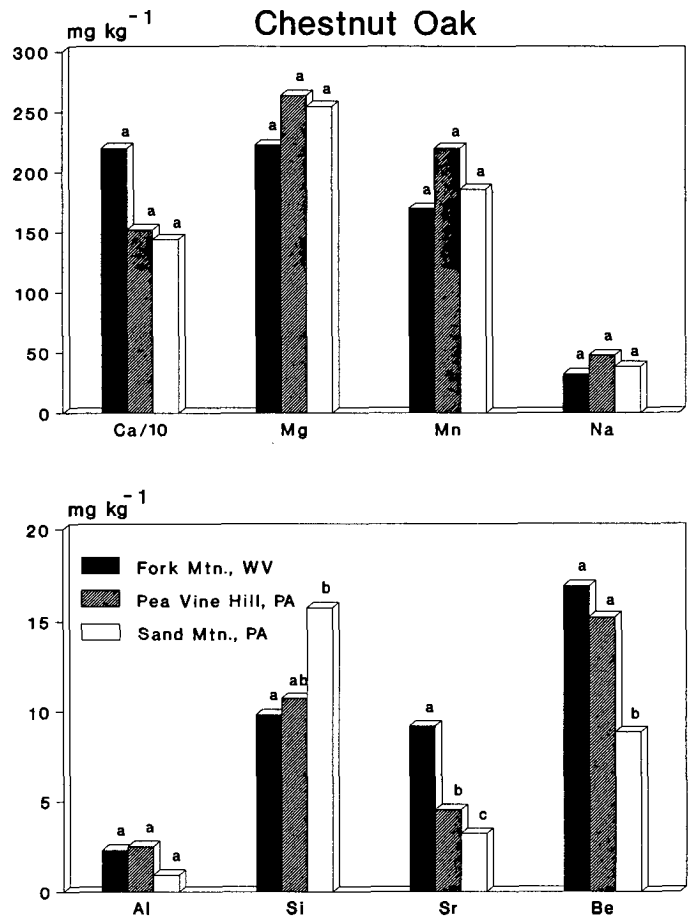


Fig. 2. Median chemical element concentrations of recent tree rings (1980-1984) in chestnut oak (*Quercus prinus* L.) at three sites. Different letters above bars indicate medians are significantly different at  $\alpha = 0.05$ .

among sites (Fig. 1). Soil pH data for the rooting zone (A and E horizons) indicate pH at Fork Mountain ranged from 4.77 to 4.92. At Pea Vine Hill and Sand Mountain, soil pH in the rooting zone was much lower, ranging from 3.49 to 4.24 (Table 1). Soil leachate chemistry for these sites indicates significant differences among sites for some of the elements measured in tree rings (DeWalle and Sharpe, 1985) (Table 2). Significant differences in Ca, Mg and Mn leachate concentrations among sites generally fit the pattern of significant differences observed in red oak tree-ring chemistry (Fig. 1). Strontium patterns in tree rings were significantly different between sites and generally mirrored Ca patterns. Romney et al. (1959) previously demonstrated the chemical similarity between Ca and Sr. Significant soil leachate differences among sites for Na and Al were not found in tree rings. Thus, recent red oak tree-ring chemistry shows significant response to varying soil pH and soil water chemistry for selected elements.

Chestnut oak tree-ring concentrations of Ca, Mg, Na, Be and Mn were not responsive to varying soil pH and leachate chemistry (Fig. 2). Only Sr content was significantly higher in tree rings at the less-acidic Fork Mountain site than at the two more-acidic Pennsylvania sites. Patterns in B-horizon soil water concentration differences among sites (Table 2) were also

Table 2. Mean annual B-horizon soil water chemistry at three of the study sites [DeWalle and Sharpe (1985)].

Element (mg L <sup>-1</sup> )	Site		
	Fork Mountain, WV	Pea Vine Hill, PA	Sand Mountain, PA
pH	4.62a†	4.43b	4.57a
Ca	6.91a	1.88b	0.68c
Mg	1.15a	0.45b	0.47b
Mn	0.27a	0.74b	0.46c
Na	0.32a	0.48ab	0.71b
Al	0.45a	2.05b	0.87c

† Means for each element followed by a different letter are significantly different among sites at ( $\alpha = 0.05$ ) using the Tukey means comparison technique (Neter et al., 1985).

not reflected in chestnut oak tree-ring chemistry. Other significant differences in chestnut oak tree-ring chemistry (Fig. 2) could not be correlated with soil acidity differences among sites.

Analysis of black cherry tree rings indicated that Fork Mountain had significantly higher Ca, Sr, and Be concentrations and significantly lower Mg, Mn, and Na concentrations compared to the more-acidic Pea Vine Hill site (Fig. 3). These tree-ring chemical differences match soil water differences between sites for Ca and Mn, but not for Mg, Al, and Na (Table 2). Differences in tree-ring concentrations between less-acidic and more-acidic sites were greater for black

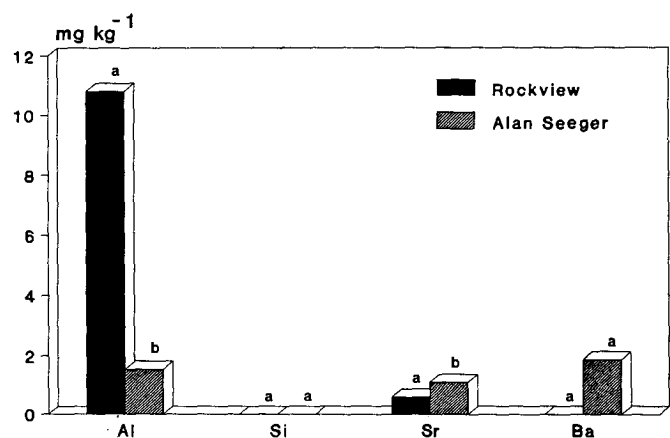
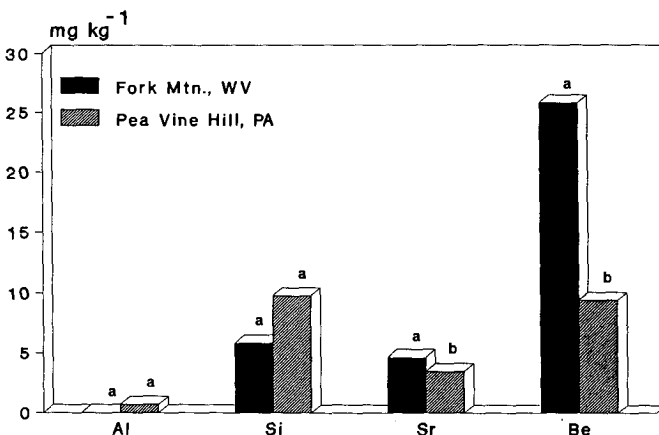
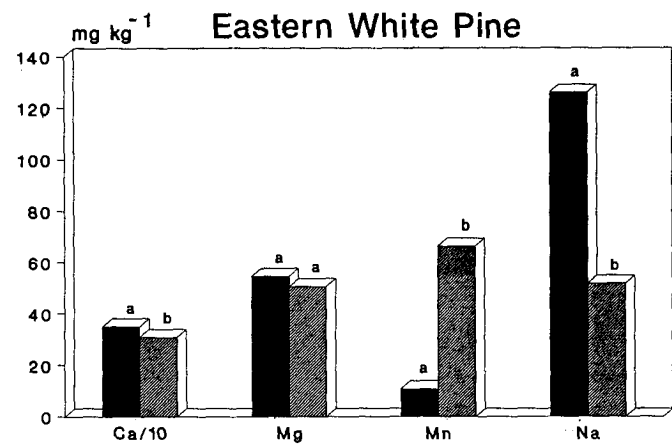
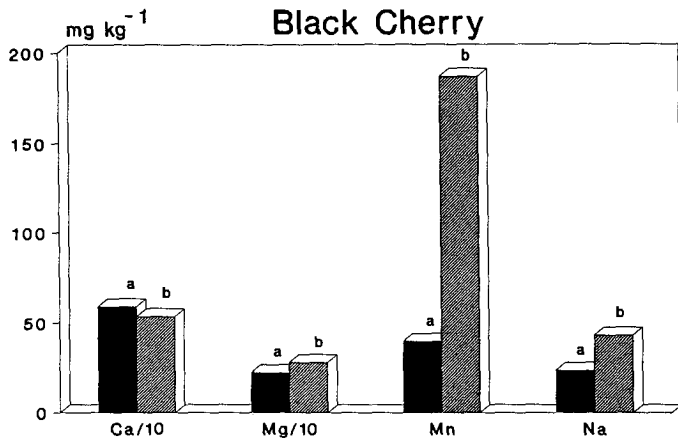


Fig. 3. Median chemical element concentrations of recent tree rings (1980-1984) in black cherry (*Prunus serotina* Ehrh.) at two sites. Different letters above bars indicate medians are significantly different at  $\alpha = 0.05$ .

Fig. 4. Median chemical element concentrations of recent tree rings (1980-1985) in eastern white pine (*Pinus strobus* L.) at less-acidic Rockview and more-acidic Alan Seeger sites. Different letters above bars indicate medians are significantly different at  $\alpha = 0.05$ .

cherry than for red or chestnut oak. Thus, black cherry may be the most sensitive to soil acidity of the three species tested at these sites.

Data from pignut hickory, eastern white pine, and eastern hemlock were also compared between two sites with differing soil acidity (Rockview = less acidic; Alan Seeger = more acidic). Figures 4, 5, and 6 illustrate the tree-ring chemical composition of the three species between the two study sites. Recent tree-ring chemistry for all three species showed consistently higher Mn, Sr, and Ba concentrations at the more-acidic Alan Seeger site than at the less-acidic Rockview site. In the two coniferous species Ca and Al were significantly higher at the less acidic Rockview site.

Results from the second study also show that soil chemistry was related to element concentrations in recent tree rings. Depending upon the tree species, more acidic soils with lower leachate concentrations of base cations (Ca and Mg) and higher concentrations of Mn produced similar patterns in tree-ring concentrations. Strontium also varied with soil acidity among sites for some species.

Higher Al found in acid soil leachate did not seem to be accumulated in recent tree rings. For the two conifers, higher Al was found at the less-acidic Rockview site where soil was derived from dolomite. For

the hardwoods, Al in tree rings did not vary over a very substantial gradient of Al found in soil water. The Al and Ca results seem to agree with Shortle and Smith (1988) who suggest that Al content may not necessarily change but would block uptake of Ca to the tree.

Absolute amounts of elements available in soil from parent materials also may affect element availability for uptake without regard to soil acidity. The fact that Sr levels are actually higher at the more acidic Alan Seeger site than at Rockview for all three tree species tested (Fig. 4-6) may be due to such differences in site availability unrelated to soil acidity.

Of the six tree species tested in this experiment, only sapwood chemistry in chestnut oak and pignut hickory appears unresponsive to varying soil chemistry. Sapwood chemistry in red oak, black cherry, eastern hemlock, and eastern white pine was responsive to variable soil chemistry. Of the nine elements tested in sapwood, Sr, Ca, Na and Mn appeared to be most responsive to soil acidity variations. Magnesium, Al, Be and Ba were somewhat responsive while Si showed the least significant differences among sites.

Future studies of tree-ring chemistry and soil acidification in the Appalachian region should focus on responsive species and elements identified in this study.

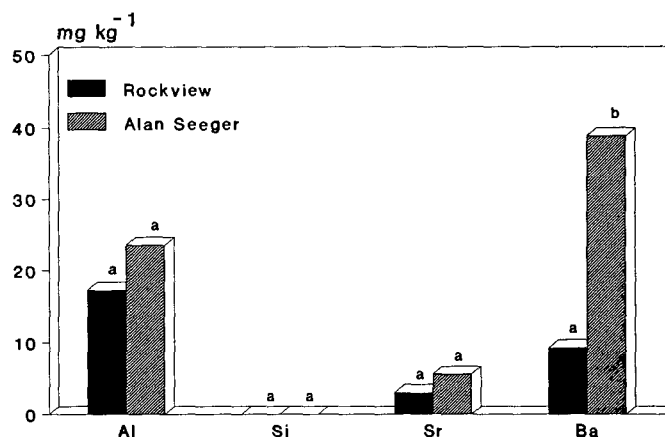
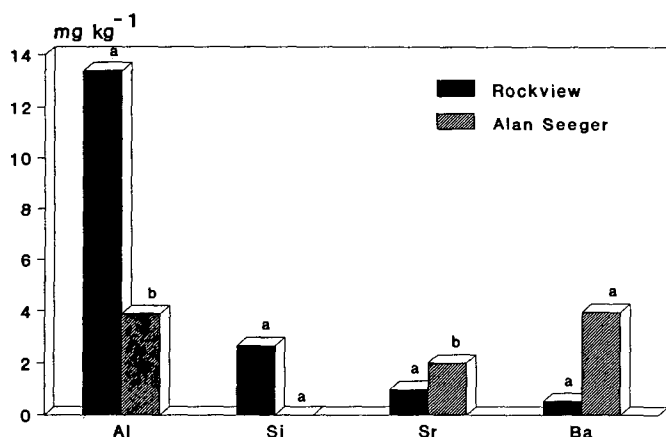
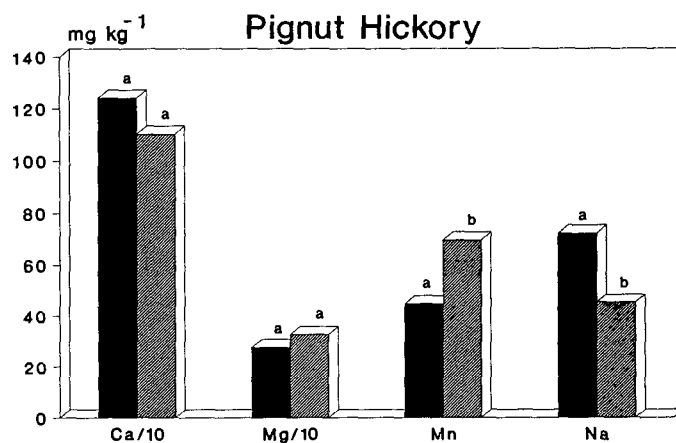
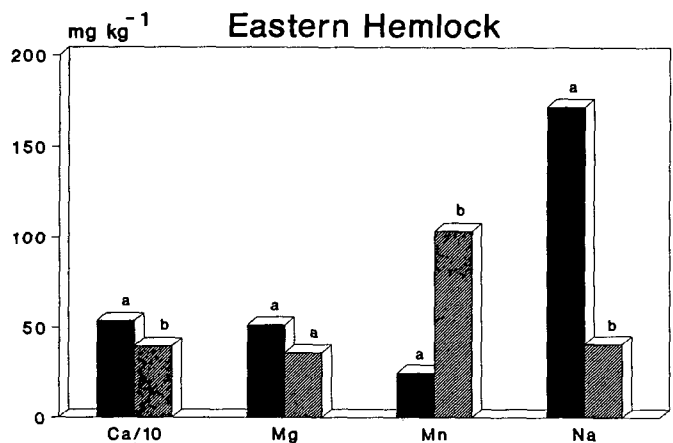


Fig. 5. Median chemical element concentrations of recent tree rings (1980-1985) in eastern hemlock (*Tsuga canadensis* L.) at less-acidic Rockview and more-acidic Alan Seeger sites. Different letters above bars indicate medians are significantly different at  $\alpha = 0.05$ .

Fig. 6. Median chemical element concentrations of recent tree rings (1980-1985) in pignut hickory (*Carya glabra* [Mill.] Sweet) at less-acidic Rockview and more-acidic Alan Seeger sites. Different letters above bars indicate medians are significantly different at  $\alpha = 0.05$ .

## ACKNOWLEDGMENTS

This research was supported by USDA Forest Service, Northeastern Forest Experiment Station; U.S. Department of Interior, Geological Survey as authorized by the Water Resources Research Act of 1984; and the Richard King Mellon Foundation.

## REFERENCES

- Baes, C.F., III. 1985. Elemental Analysis of tree rings. *Cambial Act.* 2:2-8.
- Baes, C.F., III, and H.L. Ragsdale. 1981. Age-specific lead distribution in xylem rings of three tree genera in Atlanta, Georgia. *Environ. Pollut. (Series B)* 2:21-35.
- Baes, C.F., III, and S.B. McLaughlin. 1984. Trace elements in tree rings: Evidence of recent and historical air pollution. *Science* 224:494-497.
- Barnes, D., M.A. Hamadah, and J.M. Ottaway. 1976. The lead, copper and zinc content of tree rings and bark. *Sci. Total Environ.* 5:63-67.
- Bondietti, E.A., C.F. Baes, III, and S.B. McLaughlin. 1989. Radial trends in cation ratios in tree rings as indicators of the impact of atmospheric deposition on forests. *Can. J. For. Res.* 19:586-594.
- DeWalle, D.R., and W.E. Sharpe. 1985. Biogeochemistry of three Appalachian forest sites in relation to stream acidification. *Inst. Res. Land Water Resour., Pennsylvania State Univ., University Park, PA.*
- DeWalle, D.R., W.E. Sharpe, and P.J. Edwards. 1988. Biogeochemistry of two Appalachian deciduous forest sites in relation to episodic stream acidification. *Water Air and Soil Pollut.* 40:143-156.
- Environmental Protection Agency. 1983. Methods for chemical analysis of water and wastes. EPA-600/4-79-020, Environmental Monitoring and Support Lab., USEPA, Cincinnati, OH.
- Environmental Protection Agency. 1984. Methods manual for the national surface water survey project—Phase I. Preliminary draft Environmental Monitoring Systems Lab., USEPA, Las Vegas, NV.
- Frelich, L.E., J.G. Bockheim, and J.E. Leide. 1989. Historical trends in tree-ring growth and chemistry across an air quality gradient in Wisconsin. *Can. J. For. Res.* 19:113-121.
- Guyette, R.P., B.E. Cutter, and G.S. Henderson. 1989. Long-term relationships between molybdenum and sulfur concentrations in redcedar tree rings. *J. Environ. Qual.* 18:385-389.
- Jones, J.B., Jr. 1977. Elemental analysis of soil extracts and plant tissue ash by plasma emission spectroscopy. *Commun. Soil Sci. Plant Anal.* 8:349-365.
- Legge, A.H., H.C. Kaufmann, and J.W. Winchester. 1984. Tree-ring analysis by PIXE for a historical record of soil chemistry response to acidic air pollution. *Nucl. Instrum. Methods Phys. Res.* 133:507-510.
- Lepp, N.W. 1975. The potential of tree-ring analysis for monitoring heavy metal pollution patterns. *Environ. Pollut.* 9:49-61.
- Long, R.P., and D.D. Davis. 1989. Major and trace element concentrations in surface organic layers, mineral soil, and white oak xylem downwind from a coal-fired power plant. *Can. J. For. Res.* 19:1603-1615.
- Maclauchlan, L.E., J.H. Borden, M.R. Cackette, and J.M. D'Auria. 1987. A rapid, multisample technique for detection of trace elements in trees by energy dispersive X-ray fluorescence spectroscopy. *Can. J. For. Res.* 17:1124-1130.
- McClenahan, J.R., J.P. Vimmerstedt, and A.J. Scherzer. 1989. Elemental concentrations in tree rings by PIXE: Statistical variability, mobility, and effects of altered soil chemistry. *Can. J. For. Res.* 19:880-888.
- Neter, J., W. Wasserman, and M. Kutner. 1985. *Applied linear statistical models*-2nd ed. Richard D. Irwin, Inc., Homewood, IL.
- Romney, E.M., G.V. Alexander, W.A. Rhoads, and K.H. Larson. 1959. Influence of calcium on plant uptake of Sr 90 and stable strontium. *Soil Sci.* 87:160-165.
- Sayre, R.G. 1987. Relationships between soil chemistry and tree-ring chemistry for three tree species at two forest sites in central Pennsylvania with pH 4.4 and pH 5.5 soils. M.S. thesis, Pennsylvania State Univ., University Park, PA.
- Shortle, W.C., and K.T. Smith. 1988. Aluminum-induced calcium deficiency syndrome in declining red spruce. *Science* 240:239-240.
- Symeonides, C. 1979. Tree-ring analysis for tracing the history of pollution: Application to a study in Northern Sweden. *J. Environ. Qual.* 8:482-486.