SOIL AND TREE RING CHEMISTRY CHANGES IN AN OAK FOREST

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Abstract. Changes in soil chemistry due to historic large-scale disturbances, e.g. pollution inputs, storm damage, and logging, have previously been shown to cause similar changes in the nutrient concentrations found in tree rings. Repeated soil sampling in a reference watershed at the Coweeta Hydrologic Laboratory (Otto, NC) in 1970, 1990, and 2004 showed significant decreases in cation concentrations and soil pH. It was hypothesized that historic wood nutrient concentrations could be used as a surrogate to estimate earlier soil cation concentrations. We hoped to exploit a relationship between recent soil and wood chemistry measurements to predict older soil chemistry values based on dendrochemical analysis. Oak trees (Quercus alba and Q. prinus) located in the reference watershed adjacent to long-term soil sampling plots were cored and analyzed for cation concentrations in 5-year increments. No significant relationship was found between the soil and wood chemical compositions for any given time. This indicates either that cation availability in the soil has not yet become a limiting factor for tree growth at this site, or that trees can access a source of nutrient cations other than the soil exchangeable cation pool.

Key words: acidification; aluminum; calcium; dendrochemistry; disturbance; magnesium; phosphorus; pollution; Quercus alba; Quercus prinus; soil; tree rings.

INTRODUCTION

Dendrochemistry background

Trees distinguish themselves among organisms for their longevity. Furthermore, their secondary xylem is visibly divided into yearly increments. The science of dendrochemistry was developed in order to describe and quantify correlations between the internal chemistry of trees on an annual basis and the chemical conditions prevailing in the surrounding environment, including pH, cation availability, and pollution inputs. The original goal of most dendrochemistry research was to track the effects of pollution across a long timescale as manifested in pollutant concentrations in tree rings. Whether or not the correlation between tree and environmental chemistry is valid depends on several assumptions. First, we must assume that the conditions under which the xylem was laid down actually have a consistent effect on the chemical composition of the xylem. A second necessary assumption is that the ions within the xylem are relatively static; that is, they are not radially transported throughout the tree in later years.

Disturbances such as logging have a significant effect on ecological conditions that affect tree growth. Removal of large trees releases understory plants, including saplings, from suppression due to increased sunlight and decreased competition for water and nutrients, thereby promoting plant growth. Despite the fact that some material is removed in the form of commercial timber, nutrient concentrations in the soil increase
RESULTS

Soil chemistry

A significant decrease in soil pH (Fig. 2) and soil Ca (Fig. 3) occurred between 1970 and 2004, as determined using a paired T-test (MEANS procedure, SAS software). Results are shown in Table 1. The change was most pronounced in the upper (A) soil horizon for [Ca] and in the lower (B) horizon for the pH value. Soil plots located on ridge tops also differed significantly from those along streams: namely, ridgetop plots had a lower pH and a lower [Ca] throughout the time interval studied.

Between 1970 and 1990, soil [Mg] decreased significantly in surface soils \((P=0.019)\), while increasing significantly at depth \((P=0.014)\). However, there was no significant change in [Mg] between 1990 and 2004 (Fig. 4). The ratio of Ca:Mg in the soil remained stable between 1970 and 1990, but decreased significantly within both horizons between 1990 and 2004.

Changes in soil chemistry over time were also analyzed separately for soils in ridgetop and streamside locations; each location had a group of four plots. pH decreased significantly in soils of both slope positions, but did not change significantly in the A horizon between 1970 and 1990. [Ca] did not decrease significantly in ridge soils, but it did in the A horizon of stream soils between 1970 and 1990 \((P=0.002)\). [Mg] increased in the B horizon of ridge soil plots between 1970 and 1990 \((P=0.012)\) but decreased in the A horizon of stream soils during that time \((P=0.002)\). Ca:Mg ratio did not significantly change in either ridge or stream plots.

Wood chemistry

Paired T-tests analysis showed annual growth increment was significantly greater in 1920 than in 1970 or 1990 \((P=0.032, 0.064)\). There was no significant change in Ca:Al ratio between 1920 and 1990 (Table 2 and Fig. 5); Ca:P ratios decreased significantly between 1990 and 2004 \((P=0.006, \text{Fig. 6})\). Ca:Mg ratios decreased significantly from 1970 to 1990 \((P=0.003)\) but then increased from 1990-2005 \((P=0.026, \text{Fig. 7})\). As with the soil values, ridgetop trees had significantly different chemistry than streamside trees: Ca:Al and Ca:Mg ratios were significantly greater in streamside trees \((P=0.001, 0.008)\), but Ca:P ratios were greater in ridgetop trees \((P=0.003)\).

Looking at trends separately in the ridge and stream trees, it is apparent that most of the significant change took place in the ridge trees. When analyzed separately, the decrease and subsequent increase in wood Ca:Mg ratio was significant in the ridge trees \((P=0.034)\) but not in the stream trees. However there was a trend toward a decrease in Ca:Al ratio in the stream trees from 1920-1970 \((P=0.055)\).

Fungal stains were documented on some of the extracted cores; coloring ranged from light to dark. The effect of the staining on wood chemistry is uncertain. If fungi had mobilized minerals in the wood or was analyzed along with the wood sample, the nutrient concentration values would have been affected. Infection by fungus may have added to the increased variability in older wood chemistry (see Figs. 6 and 7, for example); values prior to about 1900 became very noisy and unreliable (data not shown), possibly due to staining and the decrease in samples from this time period.
aluminum (Al). While K, Ca, and Mg are essential nutrients required for healthy plant growth, Al is toxic to plants. When base cations bind with anions, they are leached out of the soil and are no longer available for uptake by plants. Unfortunately, nutrients like Ca may be depleted by this process, but Al is practically inexhaustible in the environment of the study area due to the composition of the bedrock minerals. As acid deposition increases, the ratio of Al to Ca in the soil also increases (Shortle et al. 1995). Studies have shown that a ratio above 1 is the threshold for deleterious effects on plant growth, because at that level, root cation exchange sites begin adsorbing Al at the expense of Ca (Lawrence et al. 1995).

*Dendrochemical analysis*

Stemwood chemistry of various tree species has previously been used to reconstruct historical chemical conditions in the surrounding soil. For example, Guyette et al. (1992) conducted a dendrochemical study to examine the effects of atmospheric acid deposition in central Missouri. They used Mn concentrations in eastern redcedar (*Juniperus virginiana*) to predict historical soil pH. They concluded that there was a significant correlation between the soil pH and the wood Mn concentration. Mn is well-suited to track pH changes, since it is not overly affected by leaching and has a low mobilization factor; that is, it requires a significant decrease in pH to be taken up by tree roots.

Dendrochemical techniques have some limitations. Secondary xylem undergoes major chemical changes as it senesces and transforms from sapwood to heartwood. In mature oaks, roughly thirty of the most recent rings are still functional sapwood, while the rest has become heartwood (Cronquist 1982). Radial translocation of nutrients may invalidate the dendrochemical technique of measuring historic cation concentrations in tree rings. As wood ages, cations are often drawn out of it and transferred to new growth; a local minimum in cation concentration is often observed at the transitional zone between heartwood and sapwood (Penninckx et al. 2001). If cations are easily transmitted across rings, the concentration in wood from a given year will no longer be correlated with environmental conditions in the year when it was produced.

*METHODS*

**Soil pH and cation concentrations**

Cation concentrations and pH data were available for each of the eight soil plots for both 1970 and 1990, and soil samples were also available at each of the soil plots in 2004 and had been previously analyzed for exchangeable cation concentration. (For more detailed sampling methods, see Knoepp and Swank 1994.) Soil pH for the 2004 samples was measured by mixing 5 g of soil with 10 mL of 0.01 M CaCl\(_2\), letting it sit for thirty minutes at room temperature, and then measuring the pH with an electrode probe. This measurement was repeated for the A, B, and B2 soil horizons for three to five locations in each of the soil plots, and the values for each horizon on each plot were averaged for statistical analysis.
Increment core analysis: ICP

Fifteen white and chestnut oaks (*Quercus alba* and *Q. prinus*, respectively) were cored using a 5.5 mm increment corer in 1993 by Coweeta staff; two cores were collected from each tree. At that time, ring widths were measured for each of the two cores for all trees. Cores were sectioned into 5 year increments for cation concentration for all the trees providing data through 1993. We collected additional cores to update the data set for the following 15 years (1994-1998, 1999-2003, and 2004-2008 segments) as follows. A core was collected from each sample tree at breast height using an increment corer 5.5 mm in diameter. The cores were allowed to dry and then sectioned into five-year segments along the growth ring boundaries with a razor blade. All segments were weighed, placed in a crucible, and ashed in a muffle furnace for eight hours at 550°C. After wood sections were completely reduced to ash, they were digested in 5 mL of a 20% nitric acid solution (HNO₃) and brought to a volume of 25 mL with deionized water. Inductively coupled plasma spectrometry was used to assess the cation concentrations present within the wood for Ca, K, Mg, and Al.

We chose white oak and chestnut oak, prevalent tree species in the watershed, for several reasons. Oaks have ring-porous wood, meaning that larger-diameter vessel element cells are predominantly produced during the early part of the growing season, while smaller tracheids appear later during the summer (Zimmermann and Brown 1971). Because of this phenomenon, there is a distinct demarcation between growth rings from successive years, facilitating analysis. In addition, radial translocation of cations is minimal in oaks compared to other tree species, for example red spruce (Shortle and Smith 1995). These factors make oaks ideal for dendrochemistry studies.

Data analysis

The majority of the wood chemistry samples were collected and analyzed in 1996. Unfortunately, the data were generated by a commercial lab whose data output systems contained errors. Information needed to correct the problem was unavailable, as were the original samples. Therefore, the units for reported elemental concentrations in the wood were uncertain. As a result, we compared the ratios of the elements to one another among the trees, examining Ca:Al, Ca:Mg, and Ca:P. Normalizing the values in this way makes the units irrelevant. Furthermore, the cation concentrations from before approximately 1920 were highly variable; they were only used qualitatively. The masses of the samples collected for the years 1994-2008 were too small to get an accurate value for aluminum concentrations, so [Al] values for 1995-2005 wood chemistry are not included in this study.

We used a paired T-test to test for significant differences among years for soil and wood chemistry as well as tree annual growth increment. Regression analysis showed no significant relationships between soil exchangeable cation concentrations or soil pH and wood cation ratios, so prediction of past soil chemistry composition could not be conducted.
because a large amount of slash, consisting of residual plant matter such as leaves and small branches, is left to decompose and contributes nutrients to the soil. This occurs in several phases starting with throughfall beneath slash and followed by decaying leaves and twigs, then by larger branches and roots. We hypothesized that a past logging event would be detectable by a spike in yearly growth increment in tree cores of now-mature trees, as well as by a concurrent increase in cation concentrations in the wood (Knoepp and Swank 1997).

The initial goal of this particular study was to determine if the relationship between cation concentrations in wood and the pH and cation concentrations in the soil could be described quantitatively. If so, soil concentrations could be extrapolated backward to before the period when soil was actually sampled by using cation concentrations from older growth rings. This extrapolation could be used to predict the soil nutrient response to past disturbances within the watershed.

**History of the Coweeta basin**

The study site is located in Coweeta Hydrologic Laboratory (Otto, North Carolina), a USDA Forest Service Experimental Forest established in 1934. The landscape at Coweeta consists of a large basin with highly dissected topography; many small ridges divide the basin into numerous watersheds, each of which drains into a stream (in this case, Ball Creek). All the streams eventually drain into Coweeta Creek.

The watershed under study, reference watershed WS18, has a long, well-documented history of large-scale ecological disturbances. In 1835, during the lifetime of some of the oaks in the sampled population, a hurricane destroyed many of the trees in the Coweeta basin, and settlers farmed some of the land at higher elevations when the flat lands began to yield less crop. Most importantly, the majority of the basin was logged in 1919, removing all timber with a diameter greater than 15 inches. Shortly thereafter, the U.S. Forest Service bought the land and established the research facility; Watershed 18 remained a reference watershed and was not further disturbed. However, in the 1930s, chestnut blight struck the area. All mature chestnut trees, which had previously comprised over one-third of the dominant hardwood overstory, succumbed to the plague. All these disturbance episodes were followed by a period of higher recruitment among deciduous trees (Douglass and Hoover 1988).

The spike in growth and recruitment after the logging event is clearly visible in the dendrochronological record at the site; annual growth increment responded with a sharp increase in the years immediately following the event, then gradually decreased to previous levels after several decades (Fig. 1).

**Acid deposition and leaching**

The advent of fossil-fuel-based industry and transportation increased acid deposition from the atmosphere into the soil. Oxides of sulfur and nitrogen are discharged by the burning of coal and oil; some of it is incorporated into precipitation and ends up in the soil. As the acidic solution moves downward through the soil, the sulfate and nitrate anions increase the acidity of the soil. The anions also bind to naturally occurring base cations, such as potassium (K⁺), calcium (Ca²⁺), and magnesium (Mg²⁺), as well as
FIG. 1. Mean annual growth increment for two oak species in Coweeta Hydrologic Laboratory (Otto, NC), Watershed 18, 1780-1993.


FIG. 5. Mean wood Ca:Al ratio ±1 standard deviation, 1920-1990.

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**FIG. 7.** Mean wood Ca:Mg ratio ±1 standard deviation, 1920-2005.

**TABLE 1.** Statistical test results for soil chemistry.

<table>
<thead>
<tr>
<th></th>
<th>All soil</th>
<th>Ridge soil</th>
<th>Stream soil</th>
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<tr>
<td><strong>Ca</strong></td>
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<tr>
<td>1970-1990 horizon A</td>
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TABLE 2. Statistical test results for wood chemistry.

<table>
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**DISCUSSION**

The response of forest soils to disturbance events is consistent and predictable. A Coweeta watershed that was logged during the 1970's showed a significant increase in soil exchangeable cation concentrations immediately following the event. The concentrations stayed elevated for a substantial amount of time, dropping slowly over the next two decades (Knoepp and Swank 1997). It is very likely that a similar response occurred in the soils of WS18, starting in 1919. We expected to see a sharp increase followed by a steady decrease in the wood cation concentrations after 1920 to confirm this prediction. However, wood cation concentrations showed no significant change during that period.

Soil pH decreased significantly from 1970 to 2004 (Table 1). During this period, calcium concentration in the A (uppermost) horizon of the soil also dropped. Despite this, no concomitant decrease in tree ring calcium concentrations was observed (Table 2). We expected to find that Ca:Al ratio in tree rings would decrease with decreasing soil pH, but linear regression failed to yield a significant $R$ value; none of the other wood elemental ratios we examined were significantly related to soil chemistry.

The lack of correlation between wood and soil chemistry values is probably due to the characteristics of the local environment and its pollution history. Soil pH and calcium values recorded in the watershed are typical for Coweeta Hydrologic Laboratory: current pH values range between 4 and 5. While cation concentrations have declined, constant concentrations in wood suggest that cations are not limiting growth. Industrialization in the vicinity of the site has historically not been as extensive as other locations in the US, leading to relatively low deposition of sulfate, nitrate and other forms of pollution.
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Many of the dendrochemical studies that have found correlations between soil chemistry and wood chemistry were conducted in highly polluted areas. For example, Anderson et al. (2000) studied lead (Pb) concentrations in black oak (*Q. velutina*) stemwood in the immediate vicinity of a lead smelter in Alabama. Unsurprisingly, Pb concentrations were markedly higher in stemwood from trees that had been exposed to a high level of pollution. Other studies were done in highly industrialized areas of North America and Europe, such as *Fagus sylvatica* in Belgium (Penninckx et al. 2001), *Acer saccharum* in Ontario (Houle et al. 2007), and *Liriodendron tulipifera* in urban Ohio (McClennen and Vimmerstedt 1993). In these areas, sulfate concentrations in atmospheric deposition are much greater than in the southeastern U.S., resulting in a more pronounced soil cation decrease; this deficiency in the soil would make itself seen in xylem concentrations.

When data from all years were averaged and considered together, the chemistry of the ridge trees appeared to be more closely related to the chemistry of ridge soil than to the stream soil, although the relationship was not significant. This possible relationship provides some support for the idea that had the study been conducted in an area with a higher pollution load or with an initially more depleted nutrient pool, there may have been a detectable relationship between the chemical changes in wood and soil. However, the relationship was not significant when looking at each year individually, making the initial objective of predicting past soil nutrient concentrations impossible to assess quantitatively.

This study suggests that soil extractable calcium concentrations have not fallen beyond the point at which they become limiting to oak growth; the trees may be taking up just as much soil calcium as in previous years, despite the fact that extractable Ca has declined (Fig. 3). If this is not the case, the trees may be accessing other sources of calcium. One interesting possibility for such a calcium source, mineral weathering mycorrhizae, is suggested by van Schöll et al. (2007). Hyphae from ectomycorrhizae, which are fungi living on and around the surfaces of tree roots, can penetrate small mineral grains that are not otherwise easily weathered, forming microscopic tunnels. If the tree is experiencing a nutrient deficiency, the fungi release organic acids that help mobilize the otherwise inaccessible cations. Blum et al. (2002) also raised the possibility that mycorrhizal weathering of the common mineral apatite, Ca$_5$(PO$_4$)$_3$(OH, F, Cl), can be a vital Ca source in forest ecosystems, specifically the northern hardwood forest of North America; since the calcium is taken up directly from the minerals into the roots, it is not part of the soil exchangeable cation pool.

Physiological responses to stress by trees may also contribute to confounding results: Bukata and Kyser (2008) found that in the northern red oak (*Q. rubra*), nutrient concentrations within xylem can be highly erratic and unrelated to the bioavailability of the nutrients themselves. During historic periods of stress, concentrations of essential cations, including Ca and K, were found to increase, but chemically similar non-nutrients, such as rubidium and strontium, did not change their behavior, indicating a physiological response within the tree rather than an actual change in bioavailability.

Smith and Shortle (1996) observed that ratios of aluminum to other cations are not necessarily a useful part of wood chemistry analysis. Aluminum tends to be excluded from plant uptake at the absorbing tip of the tree root; the steeply increasing pH at the interface decreases aluminum availability for uptake to a large degree. They recommend avoiding quantitative analyses of aluminum availability to plants due to this property.

In conclusion, despite a clear decrease in soil nutrients over the past four decades at our Coweeta study site, nutrient concentrations in oak growth rings have not decreased in the same
way. The lack of a correlation between soil and wood cation concentrations at this site makes it impossible to estimate historic elemental concentrations in the soil using older tree ring values, at least in the two species studied. Conducting a similar study at a more polluted site, or one with lower soil pH and cation concentrations, would yield more convincing results and allow historic projections to be made. Research on susceptibility of wilderness areas to SO$_4$ deposition (Elliott et al. 2008) suggests that Linville Gorge Wilderness Area would be a promising spot for further research.

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LITERATURE CITED

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