ELEMENTAL ANALYSIS OF RED OAK AND LOBLOLLY PINE GROWING NEAR AN INACTIVE CHROMIUM SMELTER[1/]

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Abstract.--A pilot study of twenty-four tree cores collected from red oak (Quercus falcata Michx.) and loblolly pine (Pinus taeda L.) growing near an inactive chromium smelter north of Memphis, Tennessee is reported here. The trees sampled include growth rings formed pre-smelter, smelter, smelter-with-scrubber, and post-smelter years. The investigators used dendrochronological techniques to establish the exact years and growth trends on the cores and argon plasma emission spectrometry for elemental analysis. The elemental concentrations detected in the cores are comparable with literature reports for trees growing in pollution impacted areas. Variance in the data was used to calculate the number of samples needed for further research. The data substantiate previous observations that metal accumulation rates vary with growth rate within trees, among trees on the same site and among species.

Keywords: aluminum, chromium, smelter, argon plasma emission spectrometry, dendrochronology, elemental analysis, tree cores

INTRODUCTION

Recent research suggests that elemental analysis of tree cores can be used to track deposition of trace elements (Scherbatskoy and Bliss 1981, Baes and Ragsdale 1981, Baes and McLaughlin 1985). Several difficulties have been encountered:

1. Elements of interest are differentially mobile, that is, some remain in the growth ring in which they are deposited while others migrate into older woods.
2. Accumulation rates and mobility vary with growth rate and among species.
3. The type of equipment used was not always well suited to the elements analyzed.

Difficulties assessing elemental data which are associated with growth rates and ring age can be reduced if tree-ring dating techniques are employed. Dendrochronology or tree-ring dating establishes the exact number and year of the growth ring in a wood section with the aid of anatomical features and a technique known as crossdating (Douglass 1947, Stokes and Smiley 1968, and Fritts 1976). Once exact years have been identified the quality and quantity of growth for a specific year as well as the concentration of elements accumulated can be determined. In addition, differences in elemental concentrations related to differences in growth rates can be assessed.

Difficulties assessing elemental data because of differences among species should be reduced by species selection. In a survey of metal uptake and pathways in trees Lepp (1975) hypothesized that, based on current physiological studies, ring-porous species, such as oak, should produce more consistent and less confusing data than diffuse-porous species. Field studies suggest the use of conifers as the best bioindicators of trace metal input to forest ecosystems (Baes and McLaughlin 1985). Baes (personal communication) has found that deposition patterns of metals such as aluminum, manganese, and zinc differ greatly in hardwoods when compared with conifers.

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A pilot study of twenty-four tree cores collected from red oak (Quercus falcata Michx.) and loblolly pine (Pinus taeda L.) growing near an inactive chromium smelter north of Memphis, Tennessee is reported here. The trees sampled include growth rings formed pre-smelter, smelter, smelter-with-scrubber, and post-smelter years. This pilot study was conducted to:

1. Establish collection procedures,
2. Determine the appropriate sample size (number of samples and amount of sample needed for chemical analysis),
3. Test the chemical procedures by determining if the elemental concentrations measured are comparable to reported concentrations in wood, and
4. Observe if deposition trends change with time.

Study Area

Chrome Mining and Smelting Corporation (Chromasco) is located north of Memphis near Millington, Tennessee in the Illinois Central Woodstock Industrial Park (fig. 1). Because the prevailing winds in the Memphis area are southerly except in September, a portion of the airborne pollutants drifting north from Memphis and Chromasco were assumably deposited on the oak and pine trees sampled along transect 1 (fig. 1). Data collected by the U.S. Weather Service from 1965-1974 at Memphis shows the wind direction was from the south 41% of the time during the observed period (U.S. Dept. of Commerce 1975). These data agree with the wind rose data for 1984 shown in figure 1.

Chromasco's history of operation is pertinent to this study. Chromasco opened in 1952 as Montano-Ferro Alloy. Emission control scrubbers were not installed until 1969. The smelter continued operation with a scrubber system until 1980, at which time the furnaces were shut down due to Environmental Protection Agency (EPA) regulation violations which included visible emissions, fugitive emissions, and process particulate emissions. Three furnaces were alleged to be in violation of EPA regulations intermittently from July 1, 1972. The characteristic emissions from the Chromasco furnaces were dependent upon the product being produced. Basically, the fume composition included primarily chrome oxides from furnaces #21, #22, and #23 and silicon dioxide in addition to chrome oxides from furnace #25. Additional pollutants included carbon monoxide, ferrous oxide, manganese oxide, calcium oxide, and aluminum oxide. EPA data collected in 1971 on glass filters indicate the smelter emitted measurable quantities of metals (on a percentage basis) notably chromium, iron, aluminum, lead, and cadmium (table 1).

The soils of the study area belong to the Memphis and Memphis-Grenada-Loring associations. They are moderately well drained, silty soils (Soil Conservation Service 1970). Wiklander (1979) suggests that soils such as these with pH values above 6 and with high calcium content are less sensitive to acidic precipitation. The most immediate impact of smelter emissions is via an aerial pathway. Metal ions reaching the soil are less available to the plants because of the buffering capacity of the soils and the ability of the humus layer to complex with metal ions. Soil samples are not included in this pilot study but as the research progresses soil data will be needed to refine initial hypotheses.

METHODS

Sample Collection and Processing

The most important factors for tree selection were: location, species, age, and condition of the wood. Two cores were collected from each of five red oak trees and seven loblolly pine trees growing 1.2 km downwind of the abandoned smelter midway along transect 1 (fig. 1). The trees were chosen because of their proximity to the smelter and each other, and they are old enough to have lived during smelter activity (40-45 years old).

A teflon coated Swedish increment borer was used to remove two 5 mm cores from each tree. The borer and extractor were rinsed with a 10% solution of quarternary ammonium chloride in 2-heptanone and rinsed with acetone before insertion into the tree. This procedure removes any surface lead contamination (Baes and Ragsdale 1981). Wooden plugs were inserted into the core holes to reduce the risk of fungal invasion (Maeglin 1979). The cores were taken approximately 1.4 meters (DBH) from the ground on opposite sides of the tree. Studies of lead movement within xylem tissues suggest metal gradients may occur within the xylem making the standardization of sampling height advisable in comparative studies (Lepp 1975). The cores were inserted into plastic straws, labeled, and placed in plastic bags to prevent contamination in transport to the laboratory. Bark samples were removed with a stainless steel knife from the two core sites, placed in ziploc plastic bags, and labeled. Field notes include: date, tree location, tree diameter, core location, and species.

Samples were processed immediately or frozen until surfaced to eliminate microbial growth and/or contamination as described by McLaughlin et al. (1983) and Baes (1984). Surfacing consisted of "peeling" the samples to reduce contamination and to reveal ring detail. Each specimen was examined under 10X magnification and the skeleton-plot technique of crossdating, as described by Stokes and Smiley (1968), was used to accurately date each growth ring. After each growth ring was dated, the rings were measured to the nearest .01 millimeter. A dissecting (stereo) microscope and an Ames dial indicator attached to a horizontally moving carriage were used to

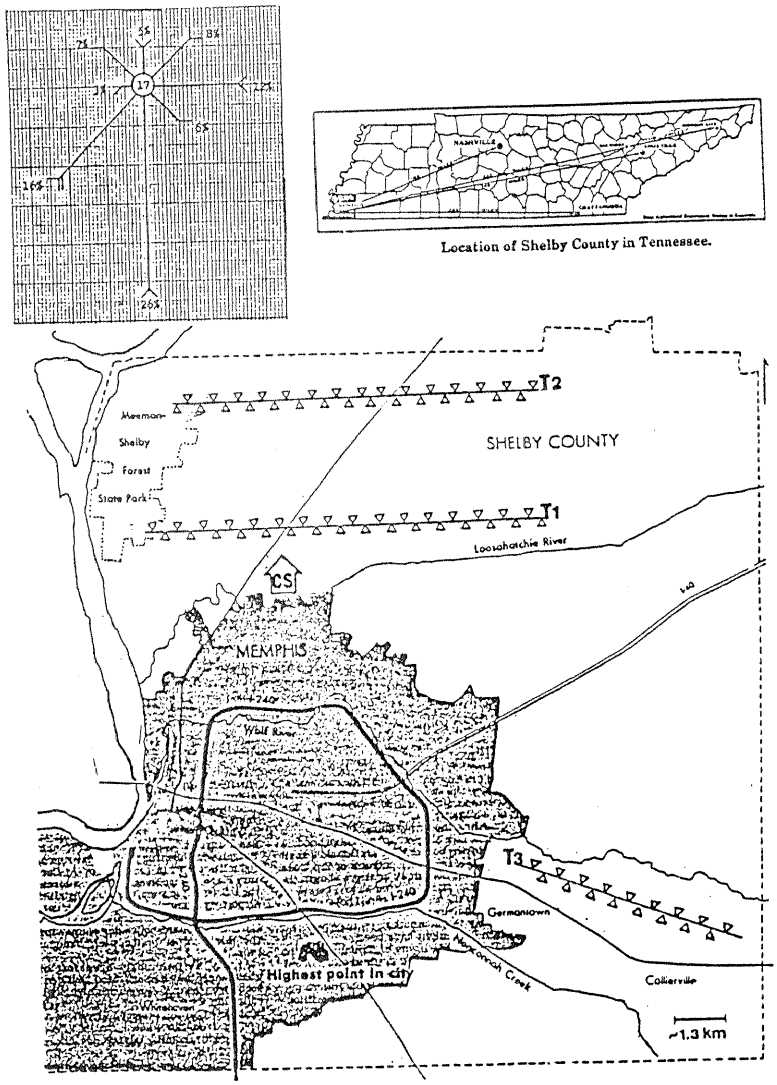

Figure 1.--Location of study area, smelter (CS) and sampling transects (T1, T2, T3). The wind rose (Feb.-Dec.) in the upper left-hand corner indicates that in 1984 the wind was from the south 48% of the time in the Memphis, Tennessee area (Sobel 1984).

measure the ring widths. Every fourth core was re-measured and an error term calculated for the repeated measures. If the error term exceeded .10 mm, the level recommended for eastern oaks (Fritts 1976), the four samples were re-measured. The ring widths for each sample were plotted and checked for errors. (See Data Analysis section below.)

Each increment core was sectioned for chemical analysis into five segments representing the time periods:

1. Pre-smelter years (1942-52)
2. Smelter years (1953-70)
3. Smelter-with-scrubber years (1971-80)
4. Post-smelter years (1981-84)
5. Cambium/Bark

Chemical Analysis

The samples were analyzed for twenty-five elements: aluminum (Al), barium (Ba), boron (B), cadmium (Cd), calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), germanium (Ge), iron (Fe), lead (Pb), lithium (Li), magnesium (Mg), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), phosphorus (P), potassium (K), silicon (Si), sodium (Na), strontium (Sr), titanium (Ti), vanadium (V), and zinc (Zn). Elemental analysis was carriedout at the Northeastern Forest Experiment Station Research Laboratory in Berea, Kentucky.

Table 1.--Chemical analysis of particulates collected from furnaces at Chromasco by the Environmental Protection Agency in 1971.

Product	FeCrSi	FeCrSi			SiMn					SiMn	Cr ore/ lime melt	HC FeCr		FeMn	50% FeSi	Si
Furnace designation	A	D			C					L	B	E		K	H	F
Furnace type	Open	Open			Open					Semi-enclosed	Open	Open		Semi-enclosed	Semi-enclosed	Open
Sample/sample point	Furnace	Baghouse inlet	Baghouse outlet	Chrome ore	Scrubber stack outlet	Scrubber water outlet	Tapping	Mn ore charge[a]	FeMn slag charge[a]	Scrubber stack outlet	Furnace	ESP conditioning tower inlet	ESP collected dust	Scrubber stack outlet	Scrubber stack outlet	Baghouse outlet
Analytical method	b	b	b	c	b	c	b	c	c	c	b	b	c	c	c	c
Chemical constituent																
SiO_2	73.7	76.4	d	8.6	d	0.095	d	14.0	14.0	d	10.3	15.0	17.2	--	d	d
Mn	0.07	0.05	0.1	0.1	14.3	0.07	21.8	d	d	1.0	0.11	0.18	0.2	3.47	--	0.002
Cr	1.41	0.44	< 0.4	30.0	0.07	e	0.1	0.01	0.115	< 0.013	15.3	14.0	4.0	< 0.008	--	0.002
Fe	0.34	0.60	1.0	5.0	0.5	0.004	1.0	3.5	9.0	< 0.064	5.2	3.66	1.0	0.21	--	0.016
Al	0.10	0.37	8.0	7.0	0.7	0.01	0.7	3.5	4.0	--	0.55	6.33	5.0	--	--	0.10
Ca	--	0.43	4.0	0.35	0.6	0.016	0.4	0.3	0.2	< 0.33	10.7	0.27	0.3	5.08	--	0.06
Mg	7.70	5.40	0.6	10.0	1.6	0.02	0.6	0.25	0.25	< 0.33	7.5	8.9	15.0	2.08	4.0	0.03
Na	--	0.23	12.7	0.01	34.5	0.055	0.05	0.35	0.3	1.64	--	4.22	15.0	1.04	40.0	0.03
Zn	0.69	0.35	0.6	< 0.02	0.7	e	0.3	< 0.02	< 0.01	< 0.044	2.81	0.93	0.5	1.39	0.4	0.003
K	--	0.25	0.9	< 0.05	23.4	0.1	6.0	2.0	1.5	2.30	--	5.95	10.0	1.46	74.0	0.17
Pb	< 0.001	--	--	< 0.01	--	f	--	< 0.01	< 0.01	0.002	0.006	--	0.1	0.113	--	0.001
Ba	--	< 0.4	< 0.4	--	--	--	--	--	--	--	--	0.11	--	< 0.03	2.0	--
Ti	--	< 0.8	--	--	--	--	--	--	--	--	--	--	--	--	--	--
Hg	< 0.05	--	--	g	--	g	--	g	g	--	< 0.05	--	g	--	--	--
Cd	< 0.005	--	--	< 0.01	--	g	--	< 0.01	< 0.01	< 0.004	0.002	--	0.01	0.19	--	f
Be	< 0.001	--	--	e	--	g	--	f	< 0.001	f	< 0.001	--	e	g	--	g
V	< 0.03	--	--	0.05	--	g	--	0.03	0.06	< 0.013	< 0.03	--	0.006	< 0.011	--	f
As	--	--	--	< 0.02	e	--	--	< 0.02	--	< 0.044	--	--	0.02	< 0.027	--	< 0.002

[a]Average of two samples

[b]Atomic absorption method.

[c]Optical emission spectrography method.

[d]Not determined. Major constituent over 25%.

[e]Less than 2 ppm.

[f]Less than 5 ppm.

[g]Less than 1 ppm.

The wood samples were placed in a drying oven for 48 hours before ashing. Then, a dried sample of 0.2 g was weighed out and placed in a crucible, heated for one hour at 200 degrees centigrade and at 600 degrees centigrade for seven hours. The resulting ash was dissolved in 25 ml of 50% HCL. (Some samples had to be heated in order to dissolve them.) The HCL mixture was diluted to 50 ml with distilled water.

The samples were then run through a Beckman Spectra Span 3B direct current plasma (DCP) emission spectrometer. The samples were further analyzed for Cd, Li, Ba, and Sr using an atomic absorption spectrophotometer. Quality control samples (EPA and National Bureau of Standards) were used to check the standards of all elements before and after the wood samples were analyzed.

Data Analysis

After the rings were measured the ring widths for each sample were plotted and checked for errors. The listing and plotting procedure of the Statistical Package for the Social Sciences (SPSS) was used.

Ring widths are not usually comparable between trees. For example, the ring width for 1960 may be much smaller on tree A than on tree B due to the advanced age of tree A. A trend line or growth curve was fitted to each ring width graph so that the value for each year can be interpreted as percentage of growth. The percentages of growth derived by fitting the growth curve are called indices and have a mean approximating one for each sample. Indices are comparable among trees. If both trees A and B show reduced growth in a particular year, they both have an index value less than one. The data is normalized by this curve fitting procedure and is suited to analysis of variance (ANOVA) (Matalas 1962).

The INDXA computer program, developed at the Laboratory of Tree-Ring Research, University of Arizona, was used to convert the values into indices, to average the indices for each year of each sample to yield a site chronology, and to calculate the statistical parameters of the site chronologies. Output from this program was checked with SPSS procedures.

Each core yielded five samples for chemical analysis - four time periods plus the bark samples. Because of the different number of years in each segment and anticipated differences in growth rates for each time period, Baes and McLaughlin's (1984) factor called the "xylem accumulation rate" was calculated by multiplying microgram of element per gram of wood x gram of wood per time period = microgram of element per time period. The mean, standard deviation, and coefficient of variation were computed for the element concentrations for each time period of each species and ANOVA used to test for significant differences. The coefficient of variation of the aluminum data was used to estimate the sample size needed to detect significant differences between time periods according to the methods of Sokal and Rohlf (1969).

RESULTS

The elemental concentrations measured for the pine and oak samples are listed in decreasing order of occurrence in table 2. The largest elemental concentrations for the pine wood samples were Ca, K, and Si and for the oak wood samples were Ca, K, and Fe. Because of the large concentration of calcium in the oak samples especially the bark, the oak samples contained a significantly higher ($p < .0001$) total mineral concentration than the pine samples. The mean concentrations of K and Cr were also significantly higher ($p = .002$) for oak wood than for pine wood. The mean concentrations of Co and Al were significantly higher for pine wood (two times greater) when compared to oak samples.

The coefficient of variation (CV) calculated for each element indicates that the concentrations measured were much more variable among the wood samples than among bark samples (table 2). The variation among the pine wood samples ranged from 129% for boron to 21% for calcium. The variation among the oak wood samples ranged from 22% for sodium to 228% for nickel. Concentrations measured for Ca, Mn, Mg, Cu, and Na were the least variable among the pine wood samples (CV less than 50%). Oak wood samples were less variable in concentrations of Na, Cu, Pb, Mn, Ti, Ca, and Cr.

Because aluminum was emitted from the Chromasco smelter and was detected in high concentrations, the CV for aluminum was used to estimate an adequate sample size to be used for further study. Using the methods described in Sokal and Rohlf (1969) and the CV for the aluminum concentrations reported here (table 2) it is estimated that 26 cores (13 trees) must be sampled for each species on each site to be 80% certain of detecting a 5% difference between the aluminum concentrations of each time period at the .05 level of significance.

Elemental concentrations of Al, B, Ca, Co, Cu, Cr, Fe, Mn, Na, Ni, Pb, Si, Ti, K, Mg, P, and Zn were plotted for the pre-smelter, smelter, smelter-with-scrubber, post-smelter, and bark samples of each core. The elements plotted for the samples fell into three groups:

1. Trend similar for the plots of almost all cores of a species: Al, B, Ca, Mn, Pb, Si, Zn, K, and P for oak; Ca, Si, Zn, K, Mn, Al, Na, Co, Ni, Pb, and Cu for pine,
2. Trend consistent for the two cores of a tree but not among trees: Cu, Cr, Fe, Na, Ni, and Ti for oak; Fe for pine, and

Table 2.--Mean (MN) and coefficient of variation (CV) for the elemental concentrations (µg of element/g of wood, dry weight).[1/]

WOOD ELEMENT	MN	CV	BARK ELEMENT	MN	CV
		PINE			
Calcium	794.30	20.59	Calcium	1950.07	32.38
Potassium	358.56	64.81	Aluminum	686.78	21.84
Silicon	243.42	116.99	Silicon	669.50	18.65
Iron	235.72	60.08	Potassium	383.29	21.52
Aluminum	230.19	87.30	Iron	351.86	26.07
Magnesium	165.44	42.37	Sodium	142.80	14.37
Zinc	139.89	76.04	Magnesium	130.93	34.73
Sodium	136.89	47.42	Phosphorus	110.86	19.53
Cobalt	109.75	104.50	Manganese	48.86	24.62
Phosphorus	87.14	53.90	Titanium	27.52	23.18
Manganese	66.28	37.81	Zinc	25.86	24.05
Chromium	37.69	80.39	Lead	20.61	36.78
Titanium	24.62	54.96	Copper	12.28	24.39
Nickel	24.21	73.19	Boron	11.64	28.95
Copper	15.92	43.59	Cobalt	8.42	75.42
Lead	10.35	83.77	Chromium	6.37	30.30
Boron	7.62	128.88	Nickel	4.43	25.51
		OAK			
Calcium	1892.91	47.57	Calcium	28054.80	42.61
Potassium	665.03	68.35	Manganese	919.70	46.17
Iron	226.66	64.74	Silicon	758.00	44.48
Silicon	206.23	60.86	Potassium	615.70	21.36
Aluminum	127.00	54.35	Aluminum	585.66	23.61
Magnesium	161.83	73.94	Iron	340.30	28.25
Sodium	142.84	21.95	Phosphorus	294.40	28.79
Zinc	136.63	65.83	Magnesium	285.60	18.27
Phosphorus	110.29	81.86	Sodium	166.51	14.63
Chromium	99.65	48.39	Lead	53.13	26.20
Manganese	50.60	34.68	Zinc	46.20	23.59
Cobalt	49.53	80.50	Titanium	39.72	18.78
Titanium	30.33	35.51	Copper	29.32	6.94
Copper	26.19	25.55	Boron	24.69	30.42
Lead	20.16	34.23	Nickel	15.86	102.08
Nickel	15.03	227.54	Chromium	12.51	14.71
Boron	6.88	101.45	Cobalt	12.09	31.35

3. Trend not consistent among cores: Co and Mg for oak; Cr, Mg, P, Ti, and B for pine.

Elements which showed a consistent trend for all cores are probably the most useful from the standpoint of site information rather than an individual tree's response. The nine elements which showed a consistent trend for the oak cores fall into two categories:

1. Increase in concentration post-smelter with the highest elemental values for the bark: K, Al, B, Ca, Mn, Pb, Si, P.
2. Increase in concentration post-smelter and lower values for bark than for outside growth rings: Zn.

The eleven elements which showed a consistent trend for the pine cores fall into four categories:

1. Increase in concentration post-smelter with the highest elemental values for the bark: K, Al, Si.
2. Increase in concentration post-smelter and lower values for bark than for outside growth rings: Zn, Ni, Pb, Na, and Cu.
3. Lowest concentrations in the scrubber and post-smelter years and highest values for bark: Ca, Mn.
4. Highest concentrations for smelter years and lowest in bark: Co.

The same concentration trend through time, that is, increase in concentration post-smelter, was evident in both the pine and oak samples for K, Al, Si, and Zn. The sample size of this pilot study is small and thus the results are viewed cautiously. However, aluminum shows a consistent concentration trend among cores and the results are described in more detail below.

Aluminum Concentrations of Oak Samples

When aluminum concentrations were plotted for pre-smelter, smelter, smelter-with-scrubber, and post-smelter years the profile for core 37-2-1 shown in figure 2a is representative for nine of the ten oak cores. Figure 2a shows a decline in concentration from pre-smelter through smelter and smelter-with-scrubber years followed by a sharp increase in aluminum post-smelter. The highest concentrations were found in the bark.

Variation in growth rates among the time periods studied is a probable cause for the increased value for aluminum concentrations post-smelter. Figure 2b shows the ring width measurements for core 37-2-1. A typical tree growth curve characterized by a decline in ring width from the inner (earliest) growth rings to the outer (most recent) is evident. When an average rate of change is calculated (method described in Dubois 1979), the smallest decline in growth rate occurs in the smelter period (-1.33%) and the largest decline occurs during the post-smelter period (-8.52%). If the average growth rate for each time period is used to adjust the elemental concentration values for each time period, i.e., the growth rate (%) is multiplied by the elemental concentration, then the weighted aluminum concentration values for core 37-2-1 appear as plotted in figure 3a.

Baes and McLaughlin's "xylem accumulation rate" was also used to adjust the aluminum values for sample 37-2-1 and plotted in figure 3b. (Microgram of element per gram of wood was multiplied times gram of wood per period to yield microgram of element per period.) The plots in figure 3a and 3b are similar. When the plots in figure 3 are compared to the unadjusted aluminum plot for the same core (fig. 2a), it is apparent that adjusted aluminum concentrations are declining from the smelter period to the smelter-with-scrubber period and the largest decline occurs from smelter-with-scrubber to post-smelter.

Further evidence is found in the data which supports a relationship between elemental concentration and growth rate. Ten oak samples were analyzed. Nine showed the same trends as illustrated by the ring width and elemental concentration graphs in figure 2, that is, a decline in growth with an increase in aluminum concentrations during the post-smelter period. However, one core (37-1-1) showed a growth increase post-smelter with a concomitant decrease in aluminum concentration. The trend in growth rate and aluminum concentration from the second core taken from the same tree as core 37-1-1 agree with all the other oak samples rather than with core 37-1-1.

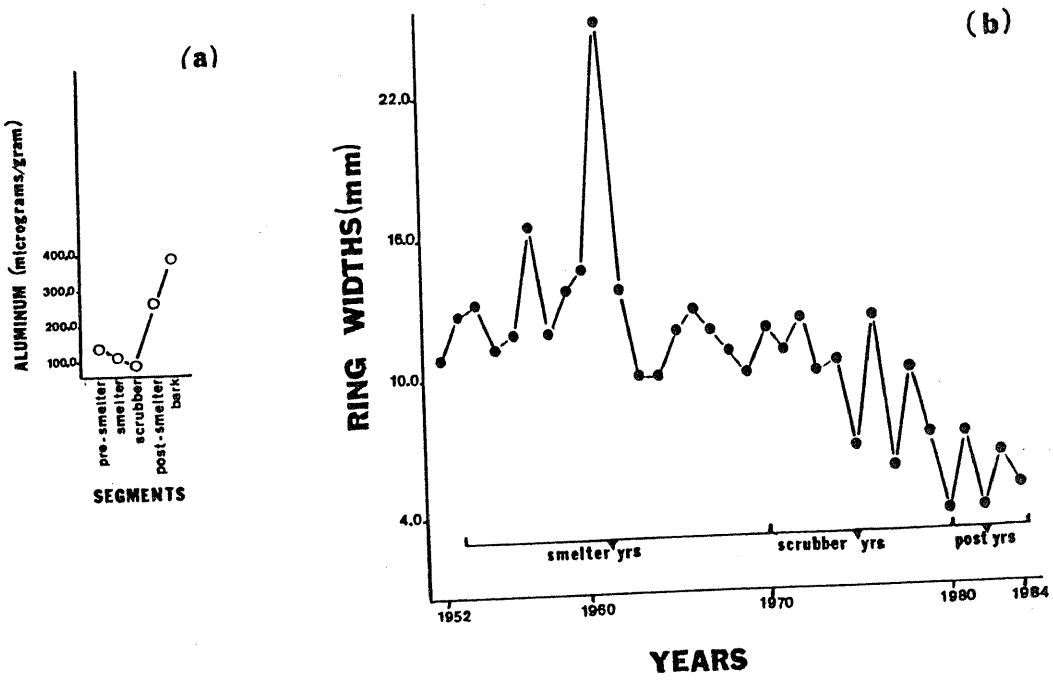

Figure 2.--Plots for oak core 37-2-1 of aluminum concentrations (a) and ring width measurements (b) for years 1952-84. (These plots are representative of nine of the ten oak cores.)

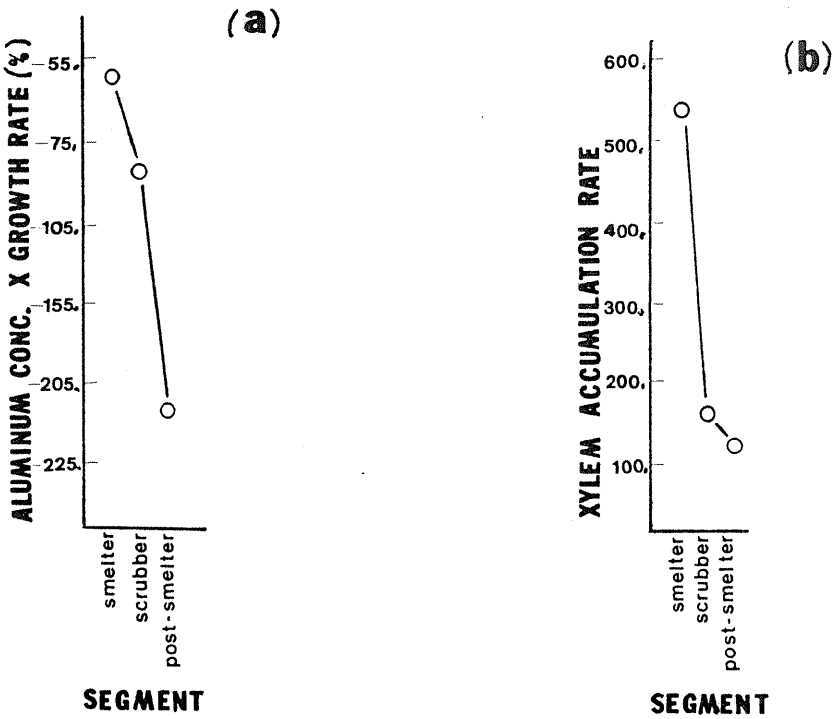

Figure 3.--Plots of aluminum concentrations for core 37-2-1 (a) adjusted by multiplying concentration times average growth rate (%) and (b) adjusted using Baes and McLaughlin's (1984) xylem accumulation rate. (Compare with unadjusted values in fig. 2a.)

Aluminum Concentrations of Pine Samples

The aluminum concentration trends for the pine samples were less consistent than those of the oak cores. Seven of the fourteen pine cores exhibited the oak concentration profile for aluminum shown in figure 2a. However, in five of the cores aluminum concentrations for the smelter period were found to be equivalent to or in one case higher than post-smelter concentrations. Again, the differences in aluminum concentrations appear to be related to differences in growth rate. A release in growth occurred in the pine trees, 1981-83, because a holding pond was dug in 1981 on the pine site which caused a rise in the water table.

Only one core, pine sample 38-7-1, of the twenty-four cores included in this pilot study showed the highest concentration of aluminum during the smelter period. The ring width chronology for this core reveals an anomalous decline in growth equivalent to post-smelter levels in the second half of the smelter time period. Many of the cores exhibited above average growth in the early smelter years and lower growth in the later smelter years but this pine core was the only core which exhibited growth as low as the lowest post-smelter years in the second half of the smelter period.

Elemental Ratios

The mean elemental concentration values for each species varies through time. Figure 4 shows the Ca/Al, Ca/Zn, and Mg/Al ratios.

Site Chronologies

The mean ring width indices chronology for the oak and pine sites are shown in figures 5b and 5c, respectively.

DISCUSSION

One objective of this pilot study was to test the collection and chemical processing procedures by determining if the elemental concentrations measured were comparable to concentrations previously reported for wood samples. All the elements detected in this study have been previously reported in wood samples (Wise et al. 1952, Smith et al. 1977). The concentrations measured for Ca, K, Mg, P, Mn, and Mo are comparable to values reported in the wood chemistry literature (Young and Guinn 1965, Schneider 1970, Choong et al. 1974a, Smith et al. 1977). However, the concentrations measured in this study for Fe, Al, Zn, Cu, Ni, and B greatly

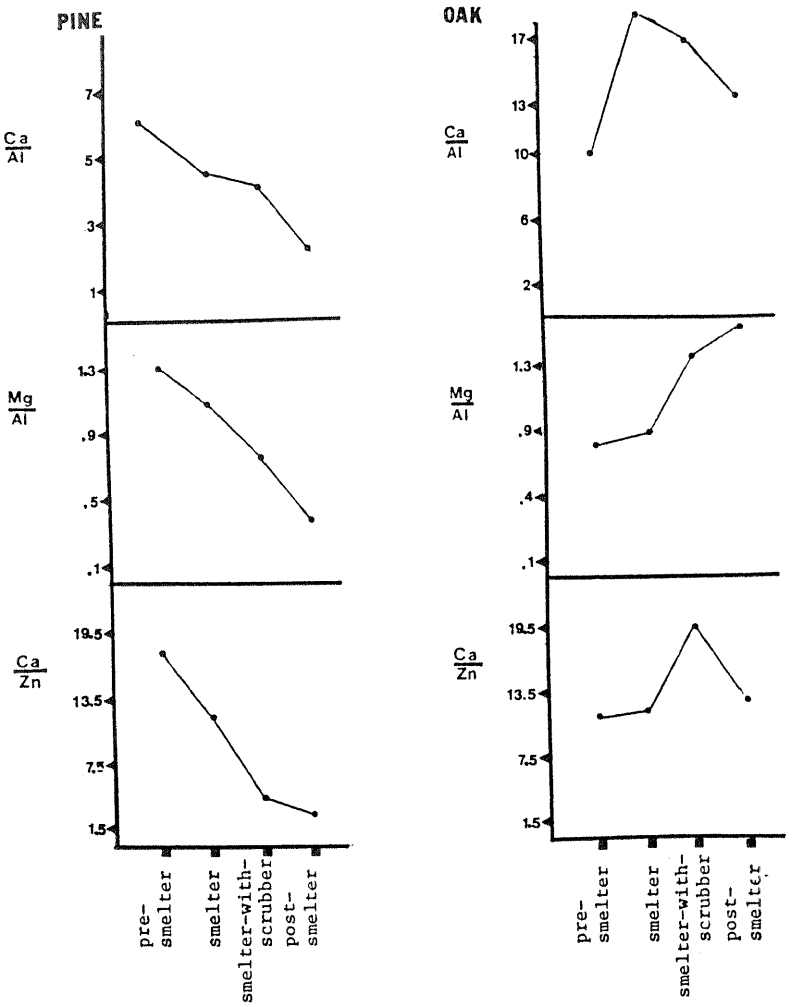

Figure 4.--Concentration ratios plotted through time: calcium/aluminum (Ca/Al), calcium/magnesium (Ca/Mg), and calcium/zinc (Ca/Zn).

exceed (3-8 times greater) the concentrations detected in these wood chemistry reports. Rather, the high concentrations for Fe, Zn, Cu, Ni, and B are comparable to concentrations measured in other pollution studies using tree cores (table 3). The aluminum concentrations reported in this study exceed literature reports (Aluminum was emitted from the Chromasco smelter which impacted the study sites).

A primary difference between the elemental concentrations measured in this study and the concentrations in wood chemistry reports is the low ranking of manganese for both the pine and oak samples (table 2). When the elements are ranked in order of occurrence, manganese concentrations rank eleventh for both species. This is in contrast to a study of Southern red oak in which manganese concentrations were higher than Al, P, and Fe and a study of loblolly pine showed manganese concentrations four to seven times greater than Na, Cu, Fe, Al, and et al. 1952, Wells et al. 1975). This indicates the degree of pollution whic impacted the study site.

Oak samples contained a significa total mineral concentration than pine primarily to the calcium concentration concentrations of Ca, N, P, and K in o compared to pines is cited as evidence higher level of mineral nutrition is r hardwoods if they are to grow at the s pines (Kramer and Kozlowski 1979). Th accumulation of calcium in oak forests discussed in-depth in a presentation b Jones during this session of the confe

The higher concentrations of Al, and P in bark when compared to bole wo concentrations which were observed in t agree with the findings of Young et al

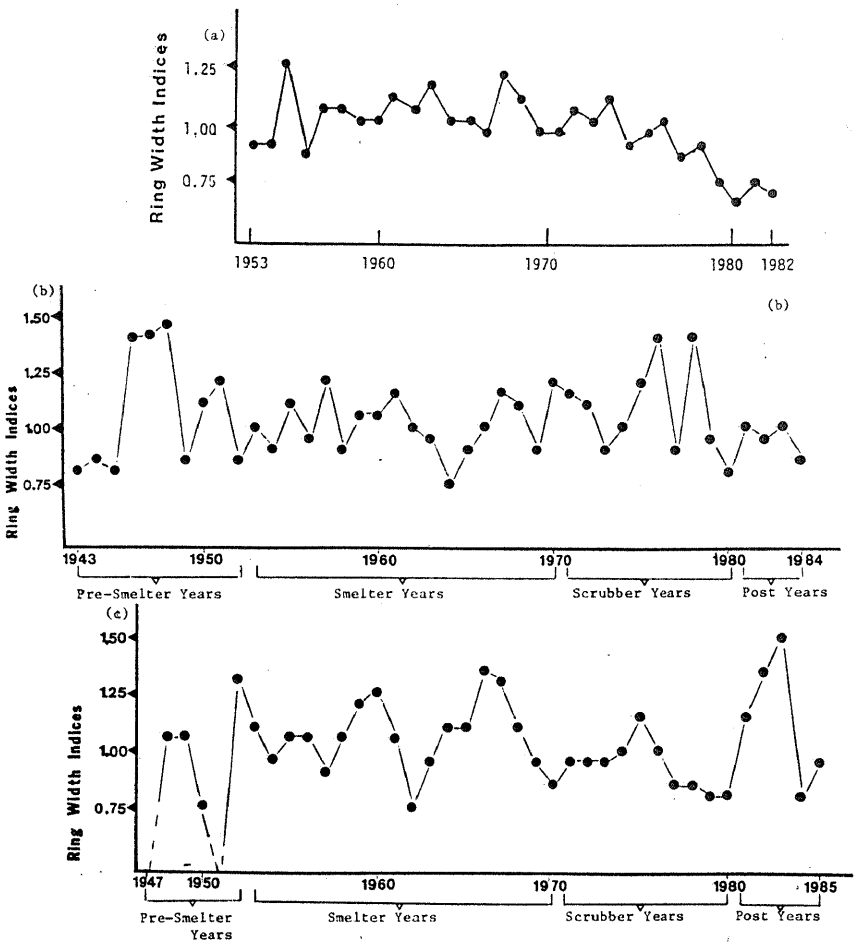

Figure 5.--Tree-ring chronologies for (a) an unimpacted pine-oak site (Bowers and Patrick 1983), (b) smelter impacted oak site, and (c) smelter impacted pine site.

However, the lower oak and pine bark concentration of zinc when compared to bole wood concentrations agrees with Young's et al. (1965) findings for hardwoods but not softwoods.

Another objective of this pilot study was to determine if elemental concentrations changed through time and if observed trends appeared to be attributed to elemental migration and/or smelter activity. There are conflicting reports in the literature concerning the trend in elemental concentrations from pith to bark. Choong et al. (1974b) found larger amounts of Na, K, Ca, Mg, Mn, Zn, and P in the pith of loblolly pine with decreasing amounts at increasing distances from the pith but the reverse trend was noted for iron. McMillin (1970) reported that growth rate and distance from the pith can affect the amount of minerals in wood. Metz and Wells (1965) reported an almost constant rate of accumulation of N, K, and P as the diameter increased with the annual rate of accumulation of the elements decreasing as the trees became larger. Variability existed among trees with potassium having the greatest variability (Metz and Wells 1965). As is the case for the pine and oak samples of this study, Smith et al. (1977) found no pattern in elemental concentrations in walnut and maples with respect to distance from the pith. Al, B, Cu, Cd, Fe, Ni, and Pb are elements which appear to be immobile once deposited in the growth rings of trees (McLaughlin et al. 1983).

When elemental concentrations of each core were plotted, temporal trends attributable to smelter activity were not clearly evident. An increase in K, Al, Si, and Zn concentrations were measured for the post-smelter time period for both the oak and pine samples. Elemental concentrations were not expected to increase post-smelter if smelter activity contributed to the amount of aluminum and zinc in the environment. The ring width data provided further insight into this unexpected phenomenon.

Table 3.--Range of values reported for aluminum, manganese, lead, and zinc in tree core studies of air pollution in the U.S. (µg element/g of wood, dry weight).

BARK VALUES	Al	Mn	Pb	Zn
Pilot Study				
Quercus falcata, yr 1985	437-840	264-1520	9-70	30-63
Pinus taeda, yr 1986	495-889	31-77	6-35	14-38
Baes et al., 1983				
Pinus echinata	200-690	150-450		27-130
Baes and McLaughlin, 1985				
Picea rubens	11-34	1100-1600		110-200
Berish and Ragsdale, 1985				
Carya sp., yr 1983		80		297
WOOD VALUES				
Pilot Study				
Quercus falcata, yrs 1942-85	49-318	29-96	7-34	35-404
Pinus taeda, yrs 1945-85	63-739	28-119	0-41	15-453
Shephard and Funk, 1975				
Pinus ponderosa, yrs 1908-71		.97-1.63		38-109
Scherbatskoy and Bliss, 1981				
Picea rubens, yrs 1900-80	2.5-17			8-21
Baes and McLaughlin, 1985				
Picea rubens	8-22	120-170		8-14
Baes and Ragsdale, 1981				
Yrs 1870-1980				
Liriodendron tulipifera			.05-.60	
Quercus alba			.03-.25	
Carya sp.			1.5-24	
Baes et al., 1983				
Pinus echinata, yrs 1943-83	5.4-36	7.4-100		3.3-260
Berish and Ragsdale, 1985				
Carya sp., yrs 1948-83	.04-.08	60-136		58-107

Not only were elemental concentrations measured but the growth rings of each core were crossdated, measured, and plotted. This allowed us to observe the changes in growth rates through time on each core and to construct site chronologies which proved indispensable to the analysis. Aluminum concentrations were found to vary inversely with growth rate. Cores which showed a decline in growth rate post-smelter contained higher concentrations of aluminum during the pre- and post-smelter period than for the smelter period. The detrimental effects of high concentrations of aluminum on biological systems is well documented but the point we are making here is not that aluminum concentrations are suppressing growth but rather that growth rate inversely effects accumulation of aluminum in the growth rings. Baes and McLaughlin (1984) also showed aluminum was accumulated in increased amounts during times of low growth.

In order to overcome the confounding effect that growth rate has on elemental concentration Baes and McLaughlin (1984) used a "xylem accumulation rate" to factor growth out of their temporal trend attributable to changes in pollutant concentrations. This method of multiplying elemental concentration per mass of wood by mass of wood per time period was also employed by Berish and Ragsdale (1985) who referred to the weighted value as the "calculated elemental burden." Using Baes and McLaughlin's (1984) method the aluminum concentrations of this pilot study were also adjusted (fig. 3b). The temporal trend in concentrations then appeared as expected, that is, highest during the smelter period and lower during the post-smelter period. Although the pilot study data show growth rate must be considered, the xylem accumulation rate may not be an appropriate method of adjusting the concentration values of this study because the time periods used do not include the same number of years and the smelter period includes the largest number of years. (The xylem accumulation rate is preferable to the average growth percentage method also employed to adjust concentration values (fig. 3a) because it is awkward to express concentrations with negative values and percentages do not have normal distributions which are required for many statistical tests.)

How else might elemental concentrations be "adjusted" or "filtered" in order to reveal temporal changes in concentration due to changes in the amount of an element in the environment rather than changes in growth rate? The most logical method is to compare concentrations from comparable trees on impacted versus unimpacted sites. When only data from impacted sites is available the temporal changes in the ratio of one element to another may prove useful.

Antonivics et al. (1971) hypothesized that Ca/Zn ratios could be used as a measure of zinc availability. This hypothesis followed Antonivic's et al. (1971) observation that zinc can be very toxic to plants at relatively low concentrations but calcium can alleviate the toxic effects of zinc and effect its uptake. Calcium has also been shown to reduce the availability of aluminum. In addition, increases in aluminum have been shown to reduce the uptake of Ca and Mg in agricultural crops (Johnson and Jackson 1964, Lance and Pearson 1969, and Huett and Menary 1980). Therefore, analysis of plant materials could show an inverse relationship between concentrations of Ca and Zn, Ca and Al, and Mg and Al. Furthermore, if the amount of Zn increased in the environment the degree of this relationship would change through time.

The Ca/Zn, Ca/Al, and Mg/Al mean concentration ratios are plotted through time for the oak and pine samples in figure 4. The pine plots in figure 4 clearly show the hypothesized inverse relationship for Ca/Zn, Ca/Al, and Mg/Al. For example, the mean zinc concentration increases sharply from the pre-smelter through post-smelter period while calcium concentrations decline. The increase in zinc is decelerating in the post-smelter period. The correlation between the mean concentration of Ca and Zn through time is significant for the pine samples ($r = -.89$, $p = .05$). The oak plots of the concentration ratios in figure 4 do not correspond to the pine plots. In the oak plot of the Ca/Al ratio, for example, both Ca and Al are increasing through time but there is a greater relative concentration increase for calcium during the smelter period. If elemental ratios from comparable unimpacted sites display different temporal trends, these ratios could prove useful in assessing smelter activity on impacted sites.

Tree ring investigations in the southeast have historically shown that a great deal of variance is due to variation within trees and among trees on the same site (Bowers 1981). Variability in aluminum concentrations which paralleled variations in growth rate indicates that variation in elemental concentrations will vary within and among trees. Thus, more than one core per tree, and an adequate number of trees per site must be sampled. Tree-ring studies also show that common growth trends occur throughout the eastern United States because of regional climate and that knowledge of these trends is necessary to properly assess local site differences (Fritts et al. 1979, Bowers et al. 1985). A reduction in tree growth is evident throughout the southeastern U.S. in the 1960's and 1977 through the 1980's. Figure 5 shows the site chronologies for the smelter impacted pine and oak sites of this study as well as for an unimpacted upland pine and oak site located approximately one hundred and twenty-five miles southeast of the smelter. All three chronologies in figure 5 show a growth decline in 1968-69, 1977, and the drought of 1980. The most obvious difference in the chronologies is the sharp increase in growth which occurs on the pine site 1981-83. This growth increase corresponds exactly with the post-smelter period but is not believed to be attributable to the cessation of smelter activity because a holding pond was installed on the pine site in 1981 which had an irrigating effect on these trees during a period of regional drought.

Further perusal of the three chronologies in figure 5 reveals the years in each time period which are below the thirty year (1953-82) growth mean for the unimpacted and impacted sites. All years of the post-smelter period were below the mean except on the impacted pine site. The period of lowest growth due to regional climate coincides with the post-smelter period and the period of highest regional growth overlaps the smelter-with-scrubber and smelter years greatly confounding not only the aluminum concentration data but our efforts to assess the smelter's impact on growth rate. The latter assessment will be aided by our future comparisons with unimpacted sites in the research area. Since the smelter time period includes both a high (early smelter years) and a low (later smelter years) growth period, the smelter period will be divided into two samples in future analysis. (This division will also make all time periods studied of comparable length.)

Because the concentrations for K, Al, Si, and Zn showed the same trends for both pine and oak samples, these elements may be the best indicators of the smelter's impact on the site rather than variations in individual tree or species response to the impact. On the other hand, individual species may be the best bioindicators for specific elements. The concentration of Co, and Al were significantly higher for pine wood than oak while chromium was found in significantly higher concentrations in the oak samples. The only "unadjusted" elemental concentration which consistently showed the highest concentration for smelter years was cobalt in the pine cores.

SUMMARY

Additional analysis is needed to determine if tree cores taken from the study area which was formerly impacted by smelter activity can be used to track changes in heavy metal deposition pre-smelter, smelter, smelter-with-scrubber, and post-smelter activity. This pilot study data;
1) shows that elemental concentrations detected in the cores are reasonable in light of literature reports of trees growing in pollution impacted areas (table 3),
2) provides information for refining future sample collection and analysis procedures,
3) substantiates previous observations that metal accumulation rates vary with growth rate and among species.

Elemental concentration trends were found to vary within and between trees of a site. Thus, more than one core per tree, and an adequate number of trees per site must be sampled. Using the methods described in Sokal and Rohlf (1969) and the coefficients of variation for the aluminum concentrations of this pilot study (table 2) it is estimated that 26 cores (13 trees) must be sampled for each species along each transect to be 80% certain of detecting a 5% difference between the aluminum concentrations of each time period at the .05 level of significance. If enough samples are collected then values may be averaged to yield the trends characteristic of the site rather than individual trees or tree radii.

An additional short core will be collected at each core site in future sampling to furnish sufficient wood mass for chemical analysis of the short post-smelter sample. This was shown to be necessary when a 5-mm diameter increment borer is used.

This study shows an appropriate research design for elemental analysis of tree cores will include measuring, crossdating, and plotting ring widths to determine changes in growth rate and to construct site chronologies. In both the pine and oak samples studied an inverse relationship between growth rate and aluminum concentration was apparent. The elemental concentrations changed through time and the trends were consistent for K, Al, Si, and Zn within trees, among trees, and between species. However, these elemental concentrations increased post-smelter. This unexpected result appears to be related to growth rate. (When growth rate was used to "adjust" the concentration values the concentrations were highest during the smelter period and lowest during the post-smelter period.)

The two species studied differed significantly in elemental concentrations. For many of the elements studied the change in concentration through time also differed between species. However, unlike Baes' findings (personal communication), these data showed a similar trend for both oak and pine in aluminum and zinc deposition. Baes has indicated that deposition of aluminum and zinc differ greatly in hardwoods when compared to conifers.

LITERATURE CITED

Antonivics, J., A. D. Bradshaw, and R. G. Turner.
1971. Heavy metal tolerance in plants. in J. B. Cragg (ed), Adv. in Ecol. Res. 7:1-85.

Baes, C. F., III.
1984. personal communication, letter dated October 11, Oak Ridge National Laboratory. Oak Ridge, TN.

Baes, C. F., III.
1985. personal communication, letter dated November 26, Oak Ridge National Laboratory. Oak Ridge, TN.

Baes, C. F., III, and S. B. McLaughlin.
1984. Trace elements in tree rings: evidence of recent and historical air pollution. Science 224:494-496.

Baes, C. F., III, and S. B. McLaughlin.
1985. Trace metal uptake and accumulation in trees as affected by environmental pollution. Publication 2571, Environmental Sciences Div., Oak Ridge Natl. Lab. Presented at the NATO Advanced Research Workshop on the Effects of Acidic Deposition on Forests, Wetlands, and Agricultural Ecosystems, May 12-17, 1985, Toronto, Canada. 19 p.

Baes, C. F., III, S. B. McLaughlin, and T. Hagan.
1983. Multielemental analysis of tree rings: temporal accumulation patterns and relationships with air pollution. Symp. on air pollution and the productivity of the forest. October 4-5, 1983. Washington, D.C. 13 p.

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. Ser. B 2:21-35.

Berish, C. W., and H. L. Ragsdale.
1985. Chronological sequence of element concentrations in wood of Carya spp. in the southern Appalachian Mountains. Can. J. For. Res. 15:477-483.

Bowers, L. J.
1981. Tree ring characteristics of baldcypress growing in varying flooding regimes in the Barataria Basin, Louisiana. Ph.D. thesis. Louisiana State Univ., Baton Rouge. 159 p.

Bowers, L. J., and W. H. Patrick, Jr.
1983. Tree ring study. in Evaluation of the effects of Corps projects on the East Fork floodplain, Tombigbee River. W. H. Patrick, Inc. Contract DACW01-82-C-0149. Mobile District, U.S. Army Corps of Engineers.

Bowers, L. J., J. G. Gosselink, W. H. Patrick, Jr., and E. T. Choong.
1985. Influence of climatic trends on wetland studies in the eastern United States which utilize tree ring data. Wetlands 5:191-200.

Choong, E. T., B. Y. Chang, and J. Kowalczuk.
1974a. Mineral content of wood and bark of sweetgum. LSU Wood Utilization Notes. No. 27, 4 p.

Choong, E. T., B. Y. Chang, and J. Kowalczuk.
1974b. Mineral composition in loblolly pine wood after fertilization. LSU Wood Utilization Notes. No. 26, 5 p.

Douglass, A. E.
1947. Precision of ring dating in tree-ring chronologies. Univ. of Arizona Bull. 27(3):21.

Dubois, E. N.
1979. Essential statistical methods for business. McGraw-Hill Book Co. N.Y. 396 p.

Fritts, H. C.
1976. Tree rings and climate. Academic Press. N.Y. 567 p.

Fritts, H. C., G. R. Lofgren, and G. A. Gordon.
1979. Variations in climate since 1602 as reconstructed from tree rings. Quat. Res. 12:18-46.

Huett, D. O., and R. C. Menary.
1980. Effect of aluminum on growth and nutrient uptake of cabbage, lettuce, and kikuyu grass in nutrient solution. Aust. J. Agric. Res. 31:749-761.

Johnson, R. E., and W. A. Jackson.
1964. Calcium uptake and transport in wheat seedlings affected by aluminum. Soil Sci. Soc. Am. Proc. 28:381-386.

Kramer, P. J., and T. T. Kozlowski.
1979. Physiology of woody plants. Academic Press. N.Y. 811 p.

Lance, J. C., and R. W. Pearson.
1969. Effect of low concentrations of aluminum on growth and water and nutrient uptake by cotton roots. Soil Sci. Soc. Am. Proc. 33:95-98.

Lepp, N. W.
1975. The potential of tree-ring analysis for monitoring heavy metal pollution patterns. Environ. Pollut. 9:49-61.

Maeglin, R. R.
1979. Increment cores - how to collect, handle, and use them. USDA Forest Serv. Res. Paper FPL 25. 19 p.

Matalas, N. C.
1962. Statistical properties of tree ring dating. Publication of the Internatl. Assn. of Scientific Hydrology 7(2):39-47.

McLaughlin, S. B., C. F. Baes, III, R. K. McConathy, L. L. Sigal, and R. F. Walker.
1983. Interactive effects of acid rain and gaseous air pollutants on natural terrestrial vegetation. Natl. Acid Precipitation Assessment Program Effects Research Rev. Feb. 21-25, 1983. 18 p.

McMillin, C. W.
1970. Mineral content of loblolly pine wood as related to specific gravity, growth rate, and distance from pith. Holzforschung 25(5):152-157.

Metz, L. J., and C. G. Wells.
1965. Weight and nutrient content of the aboveground parts of some loblolly pines. Southeast. For. Exp. Sta., U.S. Forest Serv. Res. Paper SE-17. 20 p.

Scherbatskoy, T., and M. Bliss.
1981. Studies of tree cores and metal uptake. Internal report. Dept. of Botany, Univ. of Vermont. 10 p.

Schneider, G.
1970. Micro-nutrients in a 31-year old black walnut plantation. Mich. State Univ. Agr. Exp. Sta. Res. Bull. 29. 8 p.

Sheppard, J. C., and W. H. Funk.
1975. Trees as environmental sensors monitoring long-term heavy metal contamination of Spokane River, Idaho. Environ. Sci. and Technol. 9:638-642.

Smith, S. L., H. O. Beals, B. F. Hajek, and T. C. Davis.
1977. X-ray spectroscopic analysis of six mineral elements in woody tissues. Auburn Univ. Agr. Exp. Sta. Bull. 488. 43 p.

Soil Conservation Service.
1970. Soil Survey of Shelby County, Tennessee. 51 pages plus maps.

Sobel, J. A.
1984. Wind rose data. Department of Geography, Memphis State University, Memphis, Tn.

Sokal, R. R., and F. J. Rohlf.
1969. Biometry. W. H. Freeman and Co. San Francisco. 776 p.

Stokes, M. A., and T. L. Smiley.
1968. An introduction to tree-ring dating. The Univ. of Chicago Press, Chicago. 73 p.

Turner, R.
1984. Former chemist at the Chromasco smelter who supplied personal communication and smelter effluent data.

U.S. Dept. of Commerce.
1975. Climatography of the U.S. No. 90 (1965-1974). Airport Climatological Summary. Memphis, TN International Airport.

Wells, C. G., J. R. Jorgensen, and C. E. Burnette.
1975. Biomass and mineral elements in a thinned loblolly pine plantation at age 16. U.S. For. Serv. Res. Pap. SE-126.

Wiklander, L.
1979. Ecological effects of acid precipitation. Workshop Proc., EPRI, EA-76-7-LD, SOA 77-403, England. pp. 1-24.

Wise, L. E., and E. C. Jahn (eds).
1952. Wood chemistry. Vol. I. Reinhold Pub. Co. N.Y. pp. 650-651.

Young, H. E., P. N. Carpenter, and R. A. Altenberger.
1965. Preliminary tables of some chemical elements in seven tree species of Maine. Maine Agric. Exp. Sta. Bull. 20. 88 p.

Young, H. E., and V. P. Guinn.
1965. Chemical elements in complete mature trees of seven species in Maine. unpub. report. Maine Agric. Exp. Sta., Orono, ME. 34 p.