Reprint Series
4 May 1984, Volume 224, pp. 494-497

SCIENCE

Trace Elements in Tree Rings: Evidence of Recent and Historical Air Pollution

C. F. Baes III and S. B. McLaughlin

Copyright © 1984 by the American Association for the Advancement of Science

Trace Elements in Tree Rings: Evidence of Recent and Historical Air Pollution

Abstract. *Annual growth rinks from short-leaf pine trees in the Great Smoky Mountains National Park show suppressed growth and increased iron content between 1863 and 1912, a period of smelting activity and large sulfur dioxide releases at Copperhill, Tennessee, 88 kilometers upwind. Similar growth suppression and increases of iron and other metals were found in rings formed in the past 20 to 25 years, a period when regional fossil fuel combustion emissions increased about 200 percent. Metals concentrations in phloem and cambium are high, but whether they exceed toxic thresholds for these tissues is not known.*

Our investigations with short-leaf pine *(Pinus echinata)* in East Tennessee have shown increasing concentrations of trace metals in annual growth rings since the 1950's and relatively high concentrations in the cambial area. For most elements, ring content was serially correlated with growth; however, since the 1970's metals content in rings increased while growth rate decreased. In the Great Smoky Mountains National Park (GSMNP) iron not only increased since the 1950's, as did regional increases in fossil fuel combustion emissions, but also between 1863 and 1912 when trees may have been exposed to SO_2 and combustion products from copper ore smelting at Copperhill, Tennessee. These observations suggest that multielement analysis of tree rings can provide information on temporal changes in air pollution, acid deposition, or both.

Tree rings have been used to construct records of climate (*1*), document heavy metal pollution (*2–4*), and study the relation between growth and air pollution (*5*). Now they are being used to examine the relation between growth and acid rain (*6*). Ulrich (*7*) proposed that acid precipitation increases concentrations of Al and Fe in the soil solution. If such an increase is reflected in the chemical composition of wood, then patterns of change of these and other metals in tree rings could be used to infer temporal changes in rain acidity and associated increased metals deposition from burning of fossil fuels in recent years (*8*). We

looked for evidence of increased regional atmospheric pollution in eight hardwood and six coniferous species in East Tennessee.

Trees were sampled with increment corers at several sites near Oak Ridge, Tennessee, and in the GSMNP, and multielement analysis was performed by inductively coupled plasma optical emission spectroscopy (*9*). For most elements, analytical accuracy was at least 80 percent (*10*), but our recovery of Fe (46 percent) and Al (71 percent) from National Bureau of Standards (NBS) orchard and citrus leaves and pine needles was incomplete; however, analytical precision for all metals was very good. Because precision was good and because temporal patterns of trace metals in wood were very similar among trees of a stand, confidence in temporal patterns is high. However, based on the NBS standards, the metals concentrations that we report may underestimate actual levels.

At all sites, the highest trace metals concentrations were found in living phloem plus cambium tissues. Such concentrations of Al (200 to 690 ppm), Cd (0.47 to 7.5 ppm), Mn (150 to 450 ppm), and Zn (27 to 120 ppm) in aboveground tissues of agricultural or herbaceous plants are reported to be toxic (*11*), but whether such concentrations are toxic in these tree tissues is not known. At all sites short-leaf pine are now growing at 0.6 to 0.8 mm/year, compared to initial rates of 1.6 to 7.3 mm/year (Fig. 1). However, no statistically significant (*12*) correlations between current tree growth rate and trace metals concentrations in the phloem plus cambium were found. Whether metals concentrations of such magnitude in living tree tissues are potentially of concern is not yet clear.

The highest ring concentrations were found in the most recently formed rings, and a roughly twofold increase in Fe and Ti concentrations since the 1950's at Cades Cove in the GSMNP (Fig. 1) and similar increases of Al, Cu, Mn, and Zn at all sites since the 1970's was evident. Reconstruction of SO_2 emissions upwind of Cades Cove shows a roughly 200 percent increase since the 1950's (Fig. 1). We found no statistically significant site differences in concentrations of Al, Cd, Cu, Mn, and Zn in phloem plus cambium, but found significantly higher Cu (twofold), Fe (20-fold), and Zn (40-fold) in 1978 through 1983 rings 1.4 and 16 km downwind of the 1700 MW Kingston Steam Plant than at the other Oak Ridge or GSMNP sites. This latter observation and the similarity in SO_2 emissions and increases of Fe and Ti concentration at Cades Cove underscore the potential importance of fossil fuel combustion emissions as a source of trace metals in recently formed rings.

At Cades Cove a strong growth suppression occurred from about 1863 to 1912, with the lowest rate of 0.55 mm/year around 1895. The recent (post-1960's) growth declines have been observed elsewhere and are widespread in the Northeast (*13*), but the 1863–1912 decline in the GSMNP appears to be a local occurrence. This 50-year growth suppression was also observed in the other species sampled in the GSMNP but not in short-leaf pine (*14*) at Norris, Tennessee (Fig. 1), nor in any trees near Oak Ridge. Temporally, the decline is coincident with uncontrolled emissions of SO_2 and combustion products from smelting of ore containing Fe and Cu sulfides at Copperhill, Tennessee, which contributed to the destruction of all vegetation within 16 km of Copperhill (*15*). Prevailing surface winds entering the GSMNP during the growing season follow the northeast-tending valleys of the Appalachian Mountains from the Copper Basin to the GSMNP (*16*).

Periods of growth decline, both recent and historical, have often corresponded to increased concentrations of metals such as Fe and Ti (Fig. 1). Because of this relation and the variation in growth among sites, we factored out growth by multiplying elemental concentration and growth rate (microgram of element per gram of wood × gram of wood per year = microgram of element per year), yielding "xylem accumulation rates" of elements into ring segments (Fig. 2). This measure represents annual ring content or burden (total annual accumulation) and was useful in further analyzing historical patterns.

For some elements there were strong relationships between growth and xylem accumulation rate. For Ca, Mn, and Zn at Cades Cove, the correlations between the 1833 through 1983 xylem accumulation rate and growth were positive (r^2 = 0.85, 0.90, and 0.85, respectively); Cd and Cu had weaker positive correlations between the two (r^2 = 0.51 and 0.39, respectively); and for Al, the relationship was positive before 1953 (r^2 = 0.64) but not after 1953 (r^2 = 0.026). For Fe, Mo, and Ti, poor correlations between growth and accumulation rates (r^2 = 0.062,0.28, and 0.0004, respectively) indicated either alternative influences

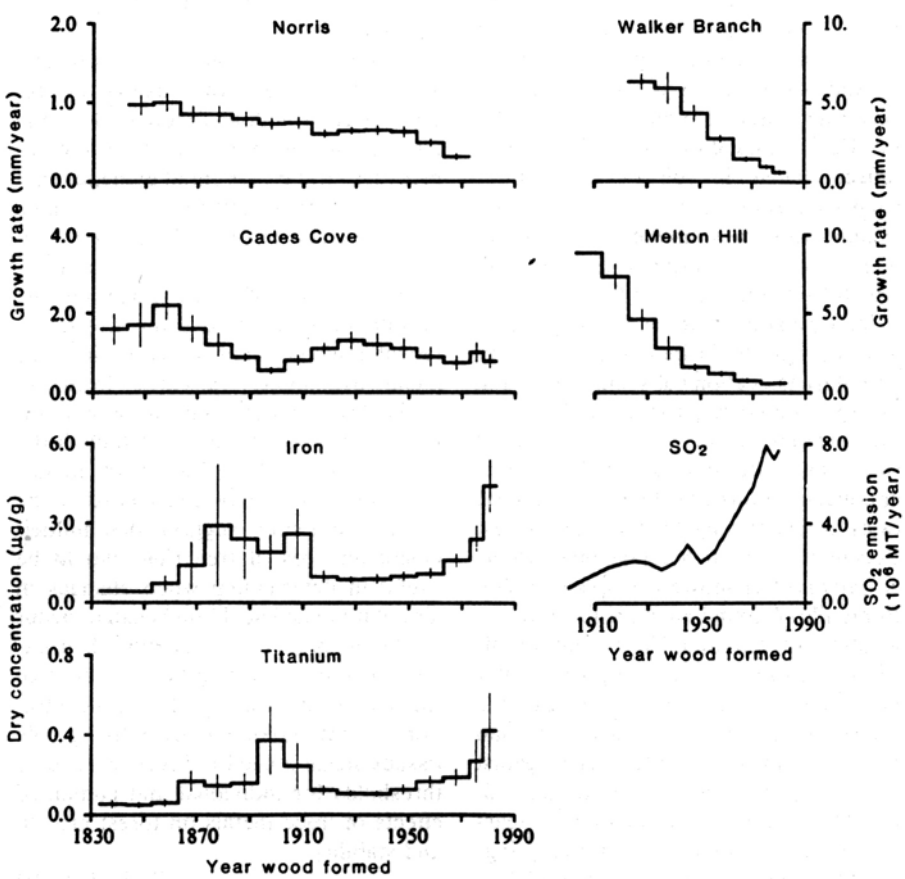
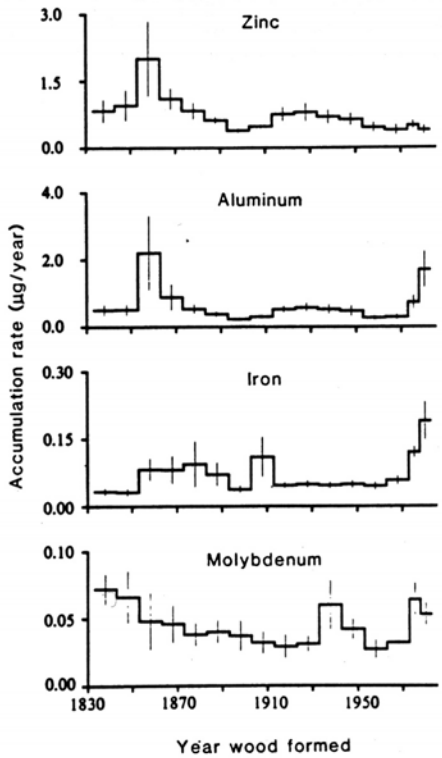


Fig. 1. Mean growth rate of short-leaf pine at four sites in East Tennessee, mean Fe and Ti concentrations in short-leaf pine at Cades Cove, Great Smoky Mountains National Park, and estimated SO_2 emissions from within 900 km southeast-southwest of Cades Cove (*8*), Error bars represent the standard error of the mean (of eight trees at Cades Cove, Walker Branch Watershed, and Melton Hill and ten trees at Norris, Tennessee); *MT*, metric tons.



Fig, 2. Mean xylem accumulation rates of four elements in short-leaf pine from Cades Cove, Great Smoky Mountains National Park. Error bars represent the standard error of the mean (of eight trees). Zinc shows a strong correlation with growth, as does Al until recent times, which may be indicative of a recent change in Al availability. Iron shows very poor correlation with growth but may be responsive to the influences of SO_2 from Copperhill. Molybdenum shows a pattern suggestive of translocation from younger to older rings.

on uptake or across-ring translocation.

At Cades Cove, an increased Fe xylem accumulation rate coincided with growth suppression during the Copperhill era and since the early 1950's. Similar increases occurred for Al and Cd since the 1960's and for Cu, Mo, and Ti since the 1970's. At the Oak Ridge sites, the same historical relation between the xylem accumulation rate and growth rate were observed, except the increases in xylem accumulation rate that are coincident with decreases in growth rate began after the 1970's for all elements, including Ca, Mn, and Zn. Such a change in the relation between growth and xylem accumulation rates parallels recent changes in availability of these trace metals to trees. For Al, Cd, Cu, and Zn, combustion sources have significantly added to natural sources in recent years, both in the Oak Ridge area (*17*) and regionally (*8*). For Fe, accumulation rate increases may reflect change in soil Fe availability, from acid deposition (*18*), because the Fe accumulation rate, unlike any other element, increased during the Copperhill era and since the late 1950's.

Interpretation of trace metals patterns in tree rings would be compromised by lateral translocation subsequent to initial incorporation in ring tissues. If there was translocation from older to younger rings, then older trees should have higher concentrations or xylem accumulation rates in recent rings than younger trees. Recent work with Virginia pine (*Pinus virginiana*) has shown the opposite (*19*). Robitaille (*4*) found no evidence of translocation of Cu and Zn in balsam fir (*Abies balsamea*) near a copper smelter in Eastern Canada. In our study, the serial correlations between growth and xylem accumulation rate argue against across-ring translocation of Al, Ca, Cd, Cu, Mn, and Zn. Translocation in years following formation of historical rings would smooth out year-to-year variability in trace-metals content, and any correlation between growth and xylem accumulation rate would likely be lost. Models of translocation from younger to older rings (20), however, suggest that the Mo xylem accumulation rate pattern at Cades Cove (Fig. 2) includes possible translocation.

In summary, the close temporal relation between Copperhill history and reduced tree growth and increased Fe xylem accumulation rate at Cades Cove provides strong inferential evidence that these trees were affected by the same smelting emissions that devastated Copperhill. Recent increases in xylem accumulation rates of many trace metals, despite declining tree growth, suggest recent regional-scale increases in trace metal availability, possibly from in-creased wet and dry deposition of fossil-fuel combustion products. Although the mechanisms and pathways of metals incorporation in tree rings need to be clarified, our study suggests that multielement analysis of tree rings would be useful in determining when changes in air pollution and acid rain began to occur and in geographically mapping their ex-tent, thereby providing key evidence of the source or sources. High concentrations of phytotoxic metals in living bole tissues signal a need to investigate toxic thresholds for individual and combined effects of trace metals on forest growth and stability.

C. F. BAES III
S. B. MCLAUGHLIN
Environmental Sciences Division,
Oak Ridge National Laboratory,
Oak Ridge, Tennessee 37831

References and Notes

1. E. R. Cook and G. C. Jacoby, Jr., *Science* **198**, 399 (1977); H. C. Fritts, *Tree Rings and Climate* (Academic Press, London, 1976); T. J. Biasing, D. N. Duvick, D. C. West, Tree *Ring Bull.* **41**, 37 (1981).
2. C. F. Baes III and H. L. Ragsdale, *Environ. Pollut. Ser. B.* **2**, 21 (1981).
3. L. Wardell and J. Larsson, *Ambio* **7**, 117 (1978); T. Suzuki, *Nippon Rin Gakkai-Shi* **57**, 45 (1975); C. Symeonides, *J. Environ. Qual.* **8**, 482 (1979).
4. G. Robitaille, *Environ. Pollut. Ser. B.* **2**, 193 (1981).
5. C. Ashby and H. C. Fritts, *Bull. Am. Meteorol. Soc.* **53**, 246 (1972); T. H. Nash III, H. C. Fritts, M. A. Stokes, *Tree Ring Bull.* **35**, 15 1975).
6. S. B. McLaughlin, D. C. West, T. J. Blasing, *Tappi J.*, in press; A. H. Johnson, T. G. Siccama, D. Wang, R. S. Turner, T. H. Barringer, *J. Environ. Qual.* **10**, 427 (1981); L. R. Ember, *C&EN* (22 November 1982); S. B. McLaughlin, D. D. Duvick, L. W. Mann, in *Proc. Air Pollut. Control Assoc.*, in press.
7. B. Ulrich, R. Mayer, P. K. Khanna, *Soil Sci.* **130**, 193 (1980); B. Ulrich, *Allg. Forstz.* **44**, 1198 (1980); *Forst Hohivirt* **21** 525 (1981).
8. A. W. Andren and S. E. Lindberg, *Water Air Soil Pollut.* **8**, 199 (1977); S. E. Lindberg, R. C. Harriss, R. R. Turner, D. S. Shriner, D. D. Huff, *Atmospheric Deposition to a Deciduous Forest Watershed* (Report ORNL/TM-6674, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1979); S. E. Lindberg, R. C. Harriss, R. R. Turner, *Science* **215**, 1609 (1982); G. Gschwandtner, K. C. Gschwandtner, K. Eldridge, *Historic Emissions of Sulfur and Nitrogen Oxides to the United States from 1900 to 1980* (Pacific Environmental Services, Inc., Durham, N. C., 1983). The SO_2 emissions in Fig. 1 are from within 900 km upwind (southeast and southwest quadrants) of Cades Cove.
9. V. A. Frassel and R. N. Kniseley, *Anal. Chem.* **46**, 1110A (1974). A 12-mm diameter corer was used, and cores were cut into 5- or 10-year sections. Sites sampled near Oak Ridge: Walker Branch Watershed, a peninsula on Melton Hill Lake, 1.4 km, and 16 km downwind of the Kingston Steam Plant (four sites).
10. Detection limits are ten times the standard deviation of background noise or roughly the following concentrations in wood (in micrograms per gram, dry weight): 0.6 Al, 1.5 Ca, 0.09 Cd, 0.32 Cu, 0.2 Fe, 0.01 Mn, 0.3 Mo, 0.4 Ti, and 0.2 Zn. Replicate analyses of NBS orchard leaves, citrus leaves, and pine needles indicate good precision, with coefficients of variation for Al, Cd, Cu, Fe, Mn, Mo, Ti, and Zn of 5.4, 22, 5.0, 10, 3.9, 19, 4.0, and 2.3, respectively; and fair accuracy with recoveries of 71, 99, 73, 46, 82, 100, 100, and 88 percent, respectively.
11. Toxicity or yield reductions in plants with aboveground dry weight tissue concentrations of > 150 ppm Zn [National Research Council, *Zinc* (University Park Press, Baltimore, 1979), 2 to 80 ppm Cd [L. E. Sommers, in *Sludge-Health Risks of Land Application* (Ann Arbor Science, Ann Arbor, Mich. 1980), p. 105], > 400 to 500 ppm Mn [L. P. Cough, H. T. Shacklette, A. A. Case, *U.S. Geol. Surv. Bull.* 1466 (1979)], and > 200 to 325 ppm Al [G, J. Ouellette and L. Dessureaux, *Can. J. Plant Sci.* **38**, 206 (1958)].
12. All tests of significance at the 0.05 level.
13. G. H. Tomlinson II, *Environ. Sci. Technol.* **17**. 246A (1983); A. H. Johnson and T. G. Siccama, *ibid.*, p. 294A.
14. These are the same trees used to form the Norris Watershed boundary chronology [E. DeWitt and M. Ames, Eds., *Tree Ring Chronologies of Eastern North America, Chronology Series IV* (Laboratory of Tree-Ring Research, University of Arizona, Tucson, 1978), vol. 1]. Norris is 68 km northwest of Cades Cove and 130 km north northeast of Copperhill.
15. Between 1854 and 1908, approximately 88 km upwind of Cades Cove, the Copper Basin of southeastern Tennessee was developed. The first copper smelter in the Ducktown Mining District was built in 1854, and between 1866 and 1879 there was rapid development of the basin. In 1891 heap roasting of ore was initiated. The heap roasting process released large quantities of SO_2 at ground level which destroyed all vegetation in the basin. By 1902 blast furnaces replaced heap roasting, and SO_2 emissions were from stacks at higher elevations. By 1908 in response to the high demand for sulfuric acid and litigation in the U.S. Supreme Court by the attorney general of Georgia to reduce caustic emissions, sulfuric acid recovery plants were in

operation, and SO_2 emissions were substantially reduced by 1910 [K. J. Seigworth, *Am. For.* **49**, 521 (1943)]
16. National Oceanic and Atmospheric Administration, *Climatic Atlas of the United States* (National Climatic Center, Asheville, N.C., 1977); F. C. Kornegay, personal communication.
17. There are five coal-fired power plants in the Oak Ridge area. Kingston burns 4.0×10^9 kg of coal per year; Bull Run, 2.3×10^9 kg/year; Y-12, 1.1×10^8 kg/year; K-25, 3.2×10^7 kg/year; and the ORNL power plant, 2.5×10^7 kg/year; the total in the Oak Ridge area is approximately 6.5×10^9 kg/year.
18. Iron is most available to plants in the ferrous form: uptake into blades of *Macrocystis* and *Phaseolus* roots and shoots has been shown to be dependent on the prereduction of Fe(III) to Fe(II); S. L. Manley, *Plant Physiol.* **68**, 914 (1981). Iron uptake is also enhanced by reduction of rhizosphere, *p*H [A. N. Sarkar and R. G. Wyn Jones, *Plant Soil* **66**,361 (1982)].
19. T. A. Hagan, unpublished work, Data included in S. B. McLaughlin, paper presented at the *U.S.–Canadian Conference on Forest Responses to Acidic Deposition*, Orono, Maine, 2 to 4 August 1983.
20. C. F. Baes III, thesis, Emory University, Atlanta, Ga. (1977)
21. We thank S. E. Lindberg, R. R. Turner, R. S. Turner, T. J. Biasing, D. N. Duvick, O. U. Braker, T. A. Hagan, D. R. Heine, and H. G. Davis for their helpful discussions and technical assistance; the Laboratory of Tree-Ring, Research, University of Arizona, for providing ring-width measurements for the Norris, Tenn., short-leaf pines; and the National Park Service for allowing us to collect samples in the Great Smoky Mountains National Park. Research sponsored by the U.S. Environmental Protection Agency under interagency agreement EPA 82-D-X0533 and with the U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation. Publication 2299, Environmental Sciences Division, Oak Ridge National Laboratory.

27 October 1983; accepted 6 March 1984