



PERGAMON

Chemosphere 49 (2002) 575–585

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Trace element concentration in tree-rings biomonitoring centuries of environmental change

Kimberly L. Padilla, Kim A. Anderson *

*Environmental and Molecular Toxicology Department, Food Safety and Environmental Stewardship Program,
Oregon State University, Corvallis, OR 97331, USA*

Received 31 December 2001; received in revised form 27 June 2002; accepted 9 July 2002

Abstract

Inductively coupled plasma mass spectrometry (ICP-MS) was used to examine trace element concentration in tree-rings over three and half centuries to assess macro-trends of environmental change. Tree-rings of a 350+ year old mammoth ponderosa pine (*Pinus ponderosa*) were analyzed for element concentration and evaluated versus local and global historical events. The ponderosa pine was located 100 miles south of the Canada/USA border and 180 miles east of the Pacific Ocean, and grew near apple orchards, a public road, and Swakane Creek in western Washington, USA. The elements tested did not all display the same time versus concentration patterns. Copper and chromium displayed cyclic concentration patterns over the last 350+ years, which appear to be associated with local events. Strontium, barium, zinc and cadmium were found to be relatively constant between the mid 1600s and the early 1800s. Strontium, barium, zinc, and cadmium then increased beginning in the early 1800s for approximately 50 years then decreased to present day 2000. Significantly, similar changes seen in Ca, Mg, and Zn in other studies have been attributed to acid rain, whereas, in our study area there is no history of anthropogenic acid rain. Most importantly, our data goes back to the mid-1600s several hundred years further back than most other studies of this nature. This additional time data provides for a better context of trend data not previously available.

© 2002 Published by Elsevier Science Ltd.

Keywords: Biomonitoring; Tree-rings; ICP-MS; Metals; Bioavailable

1. Introduction

Trees can be used as sensitive biomonitors to record local and global environmental change. Trees have been used to monitor heavy metal pollution and the effects of acidification of rainwater on forest soils (Jonsson et al., 1997). Anthropogenic, (Cutter and Guyette, 1993) as well as, natural sources (Cutter and Guyette, 1993; Ross, 1994) may contribute to accumulation of metals in the

soil. In addition, the surrounding environment is influential on element availability; for example, acid rain has a strong effect on specific element mobility in the soil and plant uptake (Acidification, 1987; Stark et al., 1989; Gartner, 1995; Hedin and Likens, 1999). Dendroanalysis, the method of analyzing tree-rings for trace metal pollution, is based on the assumption that element concentrations in the tree represent element availability in the environment in which the tree was grown (Hagemeyer, 1993; Jonsson et al., 1997). Dendroanalytical results depend on wood structure, the nature of the determined elements, and uptake pathways (Bukovac and Wittwer, 1957; Lepp, 1975; Baes and McLaughlin, 1984; Carlquist, 1988; Cutter and Guyette, 1993; Hagemeyer, 1993; Jonsson et al., 1997).

* Corresponding author. Tel.: +1-541-737-8501; fax: +1-541-737-0497.

E-mail address: kim.anderson@orst.edu (K.A. Anderson).

The main uptake pathway for elements to enter into a tree is from soil solution via the roots. Element uptake through the roots is influenced by the sapwood–heartwood concentration equilibrium, the quantity of macronutrients versus metals, ion solubility, soil type, and pH (Cutter and Guyette, 1993; Gerloff et al., 1996). Although there is little information on element uptake via foliage and penetration through the bark, these pathways do occur (Bukovac and Wittwer, 1957; Jonsson et al., 1997; Prohaska et al., 1998). Elements are selectively absorbed by plants, and are not equally mobile within the plant (Gerloff et al., 1996). Element mobility in trees is confined to the last ca. 1–7 years where the xylem is still active in water conductance. Even within the xylem, active mobility is element specific. Within the xylem it is estimated that As, Na, and Mg are considered to have higher mobility between active tree-rings, Sr, Ca, Zn, Cu, and Cr moderate mobility, and Pb, Ba, Al, and Cd lower mobility (Cutter and Guyette, 1993; Prohaska et al., 1998). A well-defined heartwood and low radial permeability increases the trees' ability to trap elements within the heartwood (Siau, 1970; Zimmermann and Grown, 1971). Although there is probably no significant transfer of elements between heartwood and sapwood, the analysis of an individual tree-ring may not pinpoint a specific year of environmental change (Sheppard and William, 1975; Cutter and Guyette, 1993; Prohaska et al., 1998). However, trees are well suited as biomonitors for macro-environmental trends, where long-term patterns of change are sought (Smith and Shortle, 1996).

Since the 1960s, there have been a number of trace analytical methods used in dendroanalysis: Colorimetric methods (Holtzman, 1970), atomic absorption spectroscopy (Robitaille, 1981), neutron activation analysis (Sheppard and William, 1975; Bondietti et al., 1990), voltametric methods (Lukasowski et al., 1988; Queirolo et al., 1990), proton induced X-ray emission (Valkovic et al., 1979), ICP atomic emission (Matusiewicz and Barnes, 1985), Laser ablation-ICP-MS (Prohaska et al., 1998), and X-ray fluorescence spectroscopy (Gilfrich et al., 1991). Typically, the above mentioned analytical methods are tedious labor intensive and/or require specialized laboratories (Hall and Pelchat, 1990; Momoshima and Bondietti, 1994). Furthermore, many trees used for dendroanalysis are only between 5 and 80 years of age (Sheppard and William, 1975; Hagemyer and Weinand, 1995; Prohaska et al., 1998). Tree species previously used for biomonitoring include *P. ponderosa* (Ponderosa pine) (Sheppard and William, 1975), *Cryptomeria japonica* (Japanese conifer) (Suzuki, 1975), *Pinus echinata* (Shortleaf pine) (Baes and McLaughlin, 1984), *Picea abies* (Mature spruce), *Cary* sp. (Hickory) (Ragsdale and Berish, 1988), and *Fagus sylvatica* (Beech) (Meisch, 1986).

Jonsson et al. (1997) studied Cd and Pb uptake in oak trees (*Quercus robur* L.) growing near Cd and Pb

emitting industries. The conclusions indicate that there was no inward radial transportation of elements from sapwood to heartwood, and little indication of outward, heartwood to sapwood, radial transportation of elements (Jonsson et al., 1997). Sheppard and William (1975) investigated ponderosa pine (*P. ponderosa*) trees (41–64 years old) growing on the banks of the Spokane River, Washington USA, which ran through mining and smelting regions (Kellogg/Coeur d'Alene, Idaho). Chromium data was in rough agreement with mining activity, and Zn data indirectly correlated with mining activity (Sheppard and William, 1975). Hasanen and Huttunen (1989) studied 40–80 year old pine trees, (*Pinus sylvestris* L.) and the effect of acid rain on element uptake by plants and forest damage. It was concluded that there was a correlation between acid rain and forest damage based on the increase in tree concentrations of Al, K, and Rb after 1950 (Hasanen and Huttunen, 1989).

Hagemyer and Weinand (1995) studied Pb uptake patterns in 5 year old Norway spruce trees and concluded that the radial distribution patterns of Pb did not directly reflect changes in soil Pb concentrations. However, the experiment was looking at rapid uptake of Pb in trees that were only 5 years of age; thus, a year to year analysis may not be practical on such a short term basis (Hagemyer and Weinand, 1995). Prohaska et al. (1998) studied 20 year old Norway spruce trees that grew near Al smelters and concluded that a particular year of environmental change could not be pinpointed down to that individual year.

Access to a viable tree core that is over 350 years old provides a unique opportunity to evaluate element trend data that until now has only been speculated beyond ca. mid-1800s. The aim of this study was to develop a robust analytical method for the analysis of a suite of elements in tree matrices and to determine the levels of 20 element isotopes in annual tree-rings. A further objective was to compare the results with local and global environmental historical changes, and to compare these results to other dendroanalytical studies. The study area is known to be free of anthropogenic acid rain.

2. Site description

The following research was conducted on a mammoth ponderosa pine (*P. ponderosa*) that fell from natural causes in 1999. This tree has a diameter of 2 m, a height of 47 m, and is approximately 350 years old. The ponderosa pine (Fig. 1, star) was located about 100 miles south of the Canada/US border and about 200 miles east of the Pacific Ocean in the Wenatchee National Forest near Entiat Washington, USA. This tree grew near apple orchards which were established in 1880, a public road (Nfd 7415), and Swakane Creek.

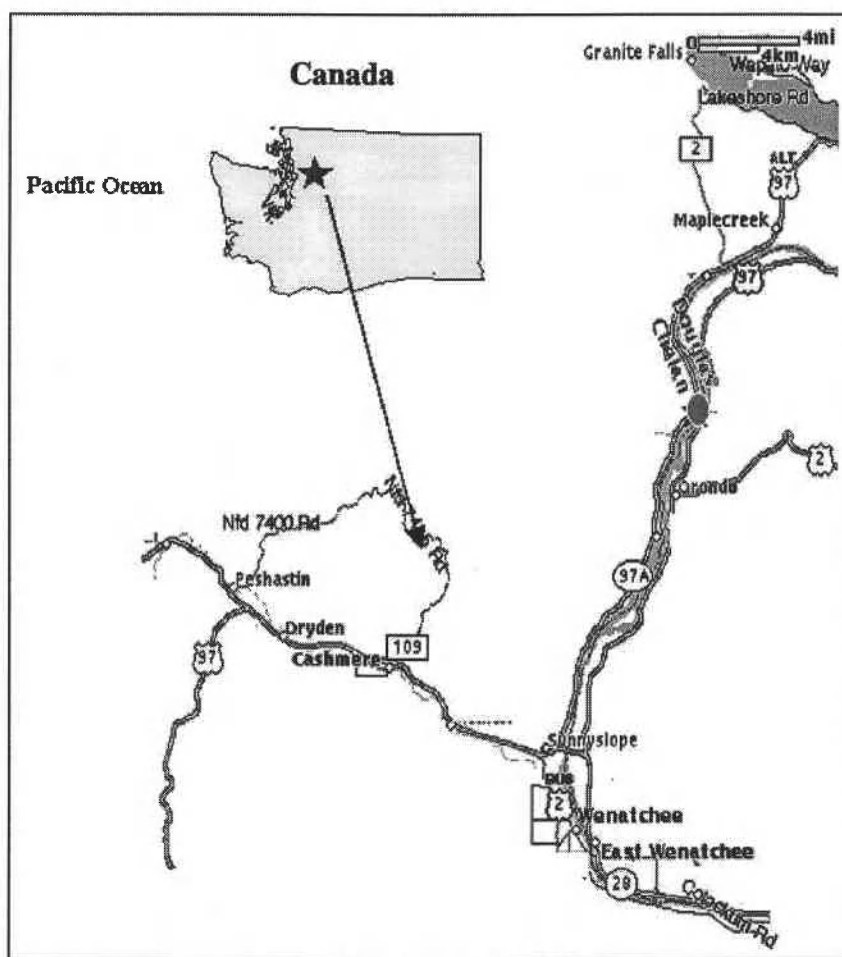


Fig. 1. Site of ponderosa pine used for analysis, Washington, USA.

The soils in the Swakane Creek area are mapped as the Mippon Series, a gravelly fine sandy loam with 0–3% slopes. These soils consist of very deep, moderately well drained soils on floodplains. Permeability is moderate (0.6–6 in./h) increasing to very rapid (>20 in./h) with depth. Runoff is slow, and the windthrow hazard is slight. The soil ranges from slightly acid to mildly alkaline (6.6–7.8 pH). There is a seasonal high water table of 30–60 inches between February and April, and occasionally there is brief (2–7 days) flooding from February to May. A series of wetlands and ponds extend the Swakane area and support a healthy beaver population (Narciso, 2000). There are three fire dates in the area: 1720, 1798, and 1826, and a possible a fire in 1785 (Shaw, 2001). A few physical symptoms of environmental stress on a tree includes loss of crown density, changes in needle size, change in branching habit, anomalies of tree growth, and degradation of the fine feeder-root system (Schutt, 1989). The ponderosa pine

analyzed in this study did not show any of the above physical stress symptoms. The average precipitation pH for this northwest region of North America is 5.3 (U.S. Geological Survey, 2001).

3. Field and laboratory methods

A cross-section of the mammoth ponderosa pine was removed approximately 4 m from the base of the tree and transferred via truck to Oregon State University. The ponderosa pine cross-section, 15 cm × 122 cm × 61 cm, was sanded, which allowed clearer identification of individual tree-ring years (Shaw, 2001). Issues of interpreting individual years were minimized by compositing tree-rings (5–10 years/sample).

The cross-sections were then placed in the fume hood to air-dry for a total of 11 days. The blocks of wood were split into small pieces to aid in drying and grinding

for sub-sampling. Several hundred grams were taken and homogenized, samples were taken from several spots representing the same rings on different areas of the tree, in general, the rings were along a 50–500 cm circumference area of the tree. A Wiley Mill was used to grind each sample into a fine homogeneous powder. Approximately 0.25 g of each sample and 3 ml of trace metal grade HNO₃ (Fisher) were digested at room temperature for ca. 72 h, then at 145 °C on a heating block (Anderson, 1996) for 4 h. Samples were diluted with 18 MΩ cm water and filtered as needed, using Acrodisc 0.45 μm syringe filters (Anderson, 1996). Internal standards of Be 9, In 115, and Bi 209 were added to all samples.

4. Instrument analysis

A VGPlasma Quad ExCell inductively coupled plasma mass spectrometer (ICP-MS) was used. The ICP-MS was configured with a mienhard nebulizer and scott spray chamber. ICP-MS instrument operational parameters are given in Table 1. Element isotopes that were tested include Cr (50, 52, 53), Cu (63, 65), Zn (64, 66), As (75), Sr (86, 88), Cd (111, 112, 114), Cs (133), Ba (138), Ce (140), Tb (159), and Pb (206, 207, 208). Calibration curves consisted of 3–5 standards for each element. Standard composites were prepared from stock solutions of Cd, As, Ce, Cr, Zn, Ba, Tb, Cs, Sr, Ni, Cu, and Pb (Alfa Aesar, Ward Hill, MA). Typical standard calibration curves consisted of a blank, 0.01, 0.1, 1.0, 5.0 and 10.0 ppb standards. The correlation coefficient (R^2) values were between 0.987 and 1.00 over the study duration. The internal standards were used to correct the mass for isotopes nearest their mass, so Be 9 was used for Cr, Cu and Zn, and In 115 was used to correct for

As, Sr, Cd, Cs and Ba, and Bi 209 was used to correct for Ce, Tb and Pb.

5. Quality control

Quality control consisted of continuing calibration checks, NIST standard reference materials (SRMs) (National Institute of Standards and Technology, NIST), and duplicates. Continuing calibration checks were within 85–115% of the true values. Duplicates were analyzed for 10% of the tree samples analyzed. Each replication consisted of two independently sub-samples from the same composite years from slightly different areas on the tree as describe above. The duplicate samples were kept in separate jars and analyzed as duplicates. Relative percent difference (RPD) (Table 2) is the difference between the results of a duplicate pair divided by the average; error bars are graphed at the average RPD between pairs for all duplicates. RPD provides a basis for statistical significance of data; when interpreting the concentration graphs, data that varied within the largest RPD was not interpreted. RPD are good with the exception of when recovered element concentrations are near the method detection limit (MDL), where the data inherently has more variability. RPD were not calculated for elements with concentrations below MDL. MDLs were determined by analyzing seven digested blanks, calculating the standard deviation (SD) then multiply the SD by the student's *t* value of 3.14, and then multiplying by the sample dilution factor. Some elements were consistently below detection limit and were not interpreted. MDLs for all other elements tested are given in Table 3. SRM matrices used were apple leaves (NIST#1515) and tomato leaves, (NIST#1573a) individual element recoveries are given in Table 3. The

Table 1
ICP-MS operating conditions

Instrument	VG Plasma Quad ExCell
Plasma forward power	1.4 kW
Coolant flow rate	13.0 l/min
Auxiliary flow rate	1.0 l/min
Nebulizer	1.0 l/min
Solution uptake rate	0.6 ml/min
Spray chamber temperature	30 °C
<i>Data acquisition</i>	
Detector mode	Pulse counting
Replicate integrations	3
Mass range	9–209
Dwell time	10 000 μs
Number of scan sweeps	100
Total acquisition time	1 min 33 s per sample

Table 2

Quality control: RPD of duplicate analysis ($n = 5$), isotopes ⁵²Cr and ⁵³Cr are at or near detection limits, and inherently there was more variability, all other element isotopes have RPD for duplicate analyses of <20%, acceptable results for analyses of this type

Isotope	RPD range of duplicates
⁵² Cr	12.6–97.6
⁵³ Cr	25.6–174.5
⁶³ Cu	1.8–18.4
⁶⁵ Cu	2.4–14.84
⁶⁴ Zn	0.27–6.67
⁶⁶ Zn	1.79–7.09
⁸⁶ Sr	0.086–10.3
⁸⁸ Sr	0.58–9.7
¹¹¹ Cd	1.07–18.4
¹¹² Cd	5.17–14.65
¹¹⁴ Cd	0.16–16.3
¹³⁸ Ba	0.04–14.16

Table 3
Quality control: Results of NIST SRM

Apple leaves (NIST#1515) <i>n</i> = 6				Tomato leaves (NIST#1573a) <i>n</i> = 6			
Isotope	Certified value ($\mu\text{g/g}$)	% Recovery	SD ($\mu\text{g/g}$)	Certified value ($\mu\text{g/g}$)	% Recovery	SD ($\mu\text{g/g}$)	MDL ($\mu\text{g/g}$)
⁵² Cr	0.3	176	0.036	1.99	92	0.21	0.02
⁵³ Cr	0.3	59	0.018	1.99	80	0.18	0.02
⁶³ Cu	5.64	92	0.62	4.7	100	0.54	0.01
⁶⁵ Cu	5.64	88	0.50	4.7	106	0.59	0.02
⁶⁴ Zn	12.5	105	2.25	30.9	116	5.48	0.64
⁶⁶ Zn	12.5	83	1.36	30.9	100	6.74	0.01
⁷⁵ As	0.038	BDL	NA	0.112	134	0.003	0.03
⁸⁶ Sr	25	131	2.89	85	101	2.04	0.80
⁸⁸ Sr	25	102	1.09	85	98	1.69	0.59
¹¹¹ Cd	0.013	BDL	NA	1.52	81	0.040	0.02
¹¹² Cd	0.013	BDL	NA	1.52	84	0.040	0.02
¹¹⁴ Cd	0.013	BDL	NA	1.52	85	0.041	0.02
¹³³ Cs	NA	NA	NA	0.053	74	0.001	0.002
¹³⁸ Ba	49	125	1.10	63	119	2.69	0.10
¹⁴⁰ Ce	3	115	0.34	2	88	0.067	0.02
¹⁵⁹ Tb	0.4	111	0.032	NA	NA	NA	0.002
²⁰⁶ Pb	0.47	73	0.092	NA	NA	NA	0.05
²⁰⁷ Pb	0.47	80	0.10	NA	NA	NA	0.05
²⁰⁸ Pb	0.47	71	0.10	NA	NA	NA	0.04

MDL = method detection limit, see text; BDL = below detection limit; NA = not available.

average percent recovered in apple leaves for all elements is 98.4%, and the average percent recovered in tomato leaves for all elements is 102.2%.

6. Results

Elements tested in tree-rings with concentrations below MDL were Cr 50, Cr 53, As 75, Cs 133, Ce 140, Tb 159, Pb 206, Pb 207, and Pb 208. Tree-ring data for all elements versus time are given in Table 4, all values are reported on a dry weight bases.

Barium 138 (Fig. 2), strontium 86 and Sr 88 generally correlate with each other in concentration versus time trends. Strontium ranges from 3 to 6 $\mu\text{g/g}$ and barium ranges from 0.7 to 1.9 $\mu\text{g/g}$. Barium and strontium concentrations remain relatively constant from mid-1600s to the early 1800s. In the early 1800s Ba and Sr concentrations increase until the mid-1800s where the maximum concentration was measured. Then at about 1850, there is a constant trend of declining Ba and Sr concentrations until the year 2000. In the case of Ba this decline represents a factor of two.

Chromium 52 demonstrates a general decline in concentration from the late 1600s to 2000. Only one isotope of chromium is reported, because chromium 50 and 53 both had high MDLs due to interferences that were not reconciled. Chromium 52 ranges in concentration from 0.08 to 0.5 $\mu\text{g/g}$. The average concentration of Cr 52 is 0.28 $\mu\text{g/g}$. Between 1686 and 1745 there is a gradual decrease in Cr concentration, nearly a factor of

two. Beginning in 1810, element concentrations generally decline to the year 2000. However, within that general decline, there are two ranges of years: 1922–1930 and 1956–1966 where Cr concentrations increase by a factor of two.

Copper 63 (Fig. 3) has an average concentration of 0.44 $\mu\text{g/g}$. Both Cu isotopes are similar in concentration versus time trends. Between the latter part of the 1600s and 2000, Cu concentrations form cyclic patterns that continually increase and decrease. Between the years 1711 and 1745 Cu concentration gradually decreases by a factor of two. During the range of years 1771–1810 and 1877–1900, Cu concentration decreases by a factor of three. Spanning the years 1901–1978, Cu concentrations remain relatively constant.

Zinc and cadmium isotopes correlate with each other in concentration versus time trends. From the late 1600s to the early 1800s (ca. 1815–1820), concentrations were fairly constant for Zn and Cd isotopes. Concentrations for both Zn and Cd then increase until the mid-1800s when concentrations begin to decline to the year 2000. Zinc 64 (Fig. 4) has an average concentration of 9.6 $\mu\text{g/g}$. At about 1815, Zn concentrations begin to increase from 6 to 20 $\mu\text{g/g}$ in the mid-1800s. In 1860/70's, Zn concentrations start to decrease from 20 $\mu\text{g/g}$ to approximately 4 $\mu\text{g/g}$ in the year 2000, a factor of five. Cadmium 114 (Fig. 5) has an average concentration of 0.041 $\mu\text{g/g}$. At about 1815, Cd concentrations increase by a factor of three in the year 1866. Cadmium concentrations then steadily decrease by a factor of three to the year 2000.

Table 4
Metal isotope concentration in tree-rings versus time

Dates/ ppm	Cr 50	Cr 52	Cr 53	Cu 63	Cu 65	Zn 64	Zn 66	As 75	Sr 86	Sr 88	Cd 111	Cd 112	Cd 114	Ba 138	Pb 206	Pb 207	Pb 208	Cs 133	Ce 140	Tb 159
1678-1685	<0.3	0.31	<0.2	0.47	0.51	12.59	8.48	<0.3	5.58	5.77	0.045	0.047	0.045	0.87	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1686-1690	<0.3	0.46	<0.2	0.57	0.60	7.24	7.02	<0.3	3.40	3.53	0.035	0.038	0.036	0.82	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1691-1695	<0.3	0.39	<0.2	0.36	0.39	10.05	6.68	<0.3	3.94	4.12	0.034	0.036	0.034	0.77	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1696-1700	<0.3	0.39	<0.2	0.30	0.33	6.58	6.42	<0.3	3.78	3.97	0.041	0.048	0.045	0.87	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1701-1705	<0.3	0.38	<0.2	0.32	0.35	6.93	6.69	<0.3	4.13	4.26	0.033	0.036	0.034	0.93	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1706-1710	<0.3	0.36	<0.2	0.47	0.49	7.16	6.94	<0.3	3.66	3.83	0.034	0.035	0.033	1.13	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1711-1715	<0.3	0.39	<0.2	0.62	0.66	7.06	6.89	<0.3	3.63	3.77	0.034	0.040	0.037	0.97	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1716-1720	<0.3	0.35	<0.2	0.59	0.62	6.84	6.64	<0.3	4.43	4.55	0.029	0.040	0.035	0.87	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1721-1725	<0.3	0.45	<0.2	0.51	0.54	8.50	7.18	<0.3	3.41	3.54	0.058	0.062	0.059	0.85	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1721-1725	<0.3	0.34	<0.2	0.47	0.50	7.95	7.70	<0.3	3.61	3.73	0.032	0.032	0.032	0.98	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1726-1730	<0.3	0.31	<0.2	0.43	0.46	7.02	6.77	<0.3	3.37	3.50	0.033	0.035	0.035	0.78	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1731-1735	<0.3	0.36	<0.2	0.50	0.54	6.28	6.08	<0.3	3.08	3.24	0.028	0.031	0.030	0.74	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1736-1740	<0.3	0.30	<0.2	0.39	0.42	6.84	6.62	<0.3	3.93	4.08	0.037	0.039	0.037	0.90	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1741-1745	<0.3	0.25	<0.2	0.28	0.32	10.72	7.17	<0.3	4.19	4.31	0.037	0.039	0.039	1.16	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1746-1750	<0.3	0.26	<0.2	0.28	0.32	8.56	7.22	<0.3	3.90	4.03	0.038	0.039	0.039	0.91	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1751-1755	<0.3	0.31	<0.2	0.44	0.47	8.02	7.72	<0.3	4.96	5.09	0.040	0.044	0.042	1.15	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1756-1760	<0.3	0.31	<0.2	0.48	0.52	7.59	7.38	<0.3	4.96	5.10	0.042	0.043	0.041	1.38	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1761-1765	<0.3	0.27	<0.2	0.47	0.51	6.56	6.36	<0.3	4.04	4.13	0.035	0.037	0.036	1.25	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1766-1770	<0.3	0.33	<0.2	0.45	0.49	6.91	6.72	<0.3	4.28	4.44	0.036	0.040	0.037	1.07	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1771-1775	<0.3	0.35	<0.2	0.69	0.73	7.34	7.15	<0.3	4.14	4.33	0.036	0.038	0.036	1.03	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1771-1775	<0.3	0.30	<0.2	0.61	0.66	6.86	6.66	<0.3	3.94	4.09	0.034	0.035	0.036	1.00	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1776-1780	<0.3	0.34	<0.2	0.59	0.62	7.57	7.31	<0.3	5.74	5.81	0.035	0.038	0.036	1.16	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1781-1785	<0.3	0.39	<0.2	0.56	0.61	7.96	7.73	<0.3	4.44	4.60	0.033	0.034	0.033	1.13	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1786-1795	<0.3	0.39	<0.2	0.38	0.43	7.27	7.05	<0.3	3.84	3.99	0.029	0.032	0.031	1.03	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1786-1795	<0.3	0.35	<0.2	0.38	0.42	7.29	7.07	<0.3	4.04	4.18	0.029	0.031	0.029	1.03	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1796-1800	<0.3	0.31	<0.2	0.31	0.36	7.60	7.33	<0.3	3.79	3.92	0.034	0.038	0.036	1.23	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1801-1805	<0.3	0.35	<0.2	0.23	0.27	7.20	6.99	<0.3	3.64	3.82	0.026	0.028	0.027	0.98	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1806-1810	<0.3	0.29	<0.2	0.15	0.19	7.98	7.74	<0.3	4.10	4.29	0.032	0.057	0.046	1.10	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1811-1815	<0.3	0.33	<0.2	0.20	0.24	12.82	8.57	<0.3	4.46	4.52	0.032	0.037	0.035	1.14	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1816-1820	<0.3	0.42	<0.2	0.59	0.64	14.58	9.73	<0.3	3.81	3.97	0.047	0.052	0.051	1.76	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1821-1826	<0.3	0.45	<0.2	0.43	0.48	14.39	9.61	<0.3	3.73	3.89	0.036	0.043	0.040	1.05	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1827-1835	<0.3	0.24	<0.2	0.30	0.34	15.65	10.51	<0.3	5.38	5.47	0.046	0.048	0.047	1.39	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1836-1845	<0.3	0.25	<0.2	0.51	0.55	14.91	10.03	<0.3	5.03	5.13	0.056	0.059	0.057	1.54	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1846-1850	<0.3	0.29	<0.2	0.50	0.54	9.01	8.68	<0.3	4.14	4.29	0.051	0.053	0.053	1.52	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1851-1855	<0.3	0.24	<0.2	0.61	0.67	15.38	10.48	<0.3	4.81	4.94	0.057	0.059	0.058	1.76	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1856-1866	<0.3	0.20	<0.2	0.67	0.74	18.46	12.24	<0.3	5.31	5.48	0.074	0.080	0.076	1.78	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1867-1876	<0.3	0.21	<0.2	0.56	0.61	20.51	13.81	<0.3	5.70	5.88	0.066	0.070	0.068	1.83	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1877-1881	<0.3	0.18	<0.2	1.02	1.10	17.25	11.61	<0.3	4.74	4.92	0.056	0.060	0.057	1.55	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1882-1891	<0.3	0.18	<0.2	0.47	0.52	17.35	11.60	<0.3	5.13	5.28	0.054	0.057	0.056	1.65	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1882-1891	<0.3	0.15	<0.2	0.39	0.45	17.00	11.39	<0.3	4.62	4.79	0.050	0.051	0.051	1.51	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002
1892-1900	<0.3	0.13	<0.2	0.37	0.43	9.58	9.31	<0.3	4.55	4.76	0.047	0.051	0.050	1.40	<0.05	<0.05	<0.04	<0.002	<0.02	<0.002

1901–1910	<0.3	0.15	<0.2	0.32	0.37	13.02	8.71	<0.3	4.43	4.57	0.049	0.051	0.050	1.30	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1911–1921	<0.3	0.14	<0.2	0.30	0.35	9.80	9.40	<0.3	4.26	4.45	0.047	0.050	0.050	1.36	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1922–1930	<0.3	0.15	<0.2	0.29	0.34	7.92	7.70	<0.3	3.78	3.98	0.046	0.053	0.050	1.33	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1922–1930	<0.3	0.44	<0.2	0.30	0.36	7.73	7.48	<0.3	3.78	3.96	0.048	0.050	0.049	1.25	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1931–1941	<0.3	0.14	<0.2	0.30	0.35	7.49	7.26	<0.3	3.45	3.67	0.043	0.045	0.044	1.05	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1942–1946	<0.3	0.08	<0.2	0.32	0.39	10.24	6.72	<0.3	3.37	3.56	0.042	0.048	0.045	0.92	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1947–1956	<0.3	0.12	<0.2	0.30	0.35	6.50	6.26	<0.3	3.20	3.42	0.035	0.040	0.038	1.20	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1957–1966	<0.3	0.26	<0.2	0.33	0.38	6.63	6.41	<0.3	3.59	3.77	0.028	0.030	0.030	0.88	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1967–1978	<0.3	0.16	<0.2	0.29	0.33	4.69	4.60	<0.3	3.06	3.26	0.027	0.029	0.028	0.82	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1979–1985	<0.3	0.16	<0.2	0.37	0.42	4.04	3.96	<0.3	2.95	3.17	0.023	0.026	0.024	0.69	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002
1986–2000	<0.3	0.14	<0.2	0.70	0.74	5.49	5.35	<0.3	3.36	3.57	0.024	0.026	0.025	0.78	<0.05	<0.05	<0.002	<0.04	<0.002	<0.002

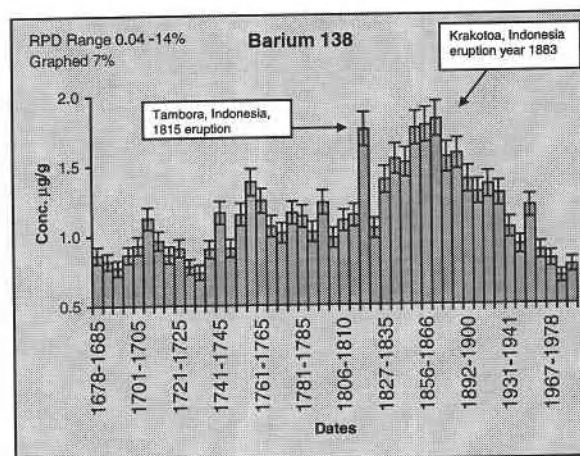


Fig. 2. Barium 138: concentration ($\mu\text{g/g}$) versus time (1678–2000), RPD = relative percent difference of duplicates.

7. Discussion

Access to the mammoth ponderosa pine provided a unique opportunity to study over 350 years of environmental change. Pre-dating the industrial revolution, anthropogenic acid rain, regional agriculture, and the automobile, this tree is Washington's 3rd largest ponderosa pine (Partridge, 1999). In March of 1999 the ponderosa fell from natural causes, which afforded us the opportunity to sample a tree (cores of trees this size are generally not possible) where 1 g (wet weight) of sample per section is needed. Ponderosa pines are native to northwest North America, thus an excellent species to use for dendroanalysis and comparison to other studies. Conifers generally have a longer life span, and are considered more sensitive to atmospheric effects than deciduous species. Coniferous trees possess year round fine foliage, which creates a high surface area for atmospheric absorption.

Most regional, local, small-scale environmental changes did not seem to impact the elemental concentrations within the tree. Arsenic, used as an insecticide in local apple orchards did not occur in the tree above our detection limits. Local road building and increases in petroleum combustion/automobiles in the region did not cause Pb to occur in the tree above our detection limits. Ore smelters in western Washington with peak emissions in the early/mid-1900s did not increase cadmium, lead, zinc, or copper in the tree core samples during this period. These elements either were constant during this period (e.g. copper), or were decreasing in concentration during this period (e.g. zinc, cadmium, chromium) (see Figs. 3–5).

Effects on forest health and element uptake within tree-rings from acid rain have been reported. Decrease in soil pH increases selective element solubility and plant

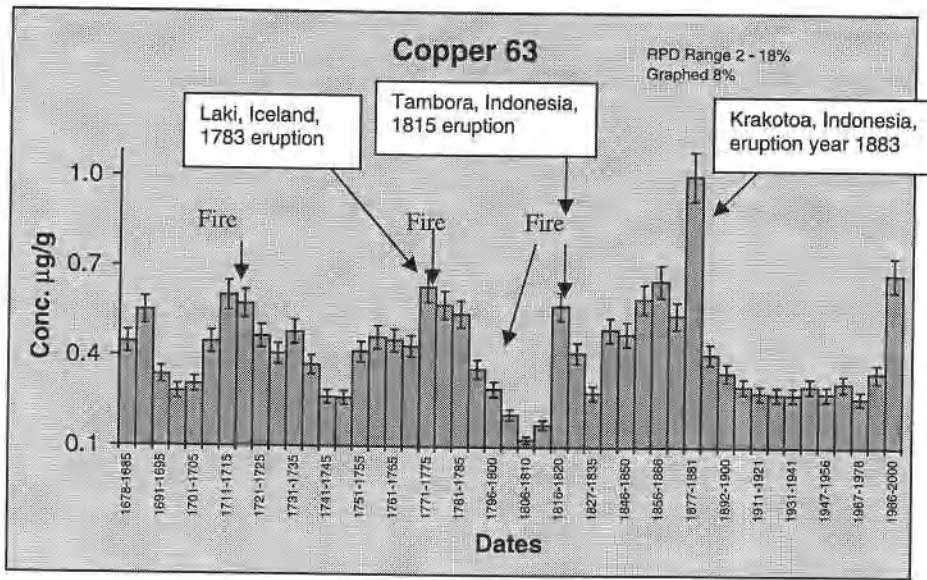


Fig. 3. Copper 63: concentration ($\mu\text{g/g}$) versus time, RPD = relative percent difference of duplicates. The local fire dates indicated with arrows in the years 1720, 1785 and 1826.

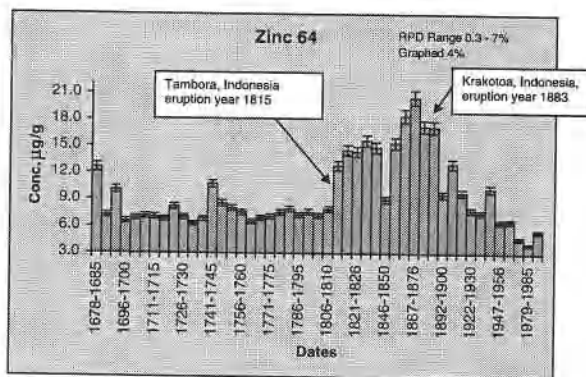


Fig. 4. Zinc 64: concentration ($\mu\text{g/g}$) versus time (1678–2000), RPD = relative percent difference of duplicates. The sharp increase in zinc concentration is associated with the volcanic eruption of the Indonesian volcano Tambora (1815), estimates of sulfuric acid aerosols from this eruption are 2×10^{11} kg.

uptake (Tyler et al., 1987) creating higher element distribution patterns in the tree (Baes and McLaughlin, 1984; Bondietti et al., 1990). It has been proposed that over time; however, prolonged exposure of soils to acid rain will eventually deplete the local ecosystem, resulting in decreasing element concentration patterns in the tree (Hedin and Likens, 1999). Concurrently, atmospheric interactions, between acidic gases and mineral bases, producing base cations (Ca^{2+} and Mg^{2+}) that neutralize acid rain at ground level have decreased. Natural reserves of base cations have been proposed to be historically decreasing, depleted by prolonged exposure to

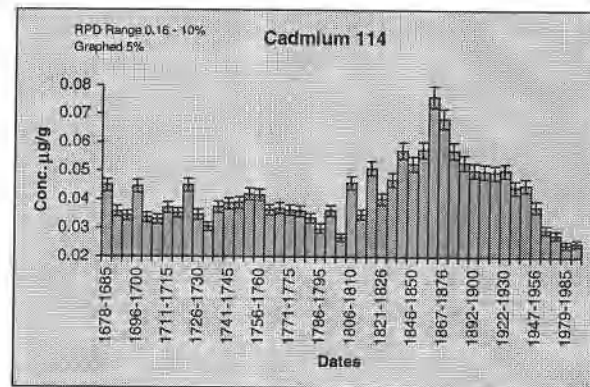


Fig. 5. Cadmium 114: concentration ($\mu\text{g/g}$) versus time (1678–2000), RPD = relative percent difference of duplicates.

acid rain over decades, thus no longer protecting forests, as in parts of (eastern) North America and Europe (Hedin and Likens, 1999). Our study area does not have conventional anthropogenic acid rain, measurements over the last few decades indicates rain averages pH 5.3 (U.S. Geological Survey, 2001), natural rain is typically pH 5.6. Our study area has not been exposed to prolonged acid rain, yet many elements have been on a steady decline in the tree-rings, for example Zn, Cd, Ba, Sr, and Cr. Although other tree-ring studies also have reported declining element concentrations over the last 50–100 years (Baes and McLaughlin, 1984; Hasanen and Huttunen, 1989; Bondietti et al., 1990), our data cannot

be explained by anthropogenic rain and/or prolonged exposure to recent (last 50–100 years) acidic rain.

The most prominent feature in the data (Zn, Cd, Ba, Sr, and Cu) is that after 150+ years (mid-1600s to early 1800s) of relatively constant element tree-ring concentrations, in ca. 1810–1820, a change begins where these elements increase in tree-rings. This trend continues for nearly 50 years (1860s) and then for the next 150 years all these elements (Zn, Cd, Ba, Sr, and Cu) have been on a steady decline. In some cases, the element concentrations are at historical lows (see Figs. 2, 4 and 5). No local regional events were found to be associated with this timing; however, the eruption of Tombora, in Indonesia in 1815 does associate with this change.

It has been estimated that the Tombora eruption of 1815 emitted 2×10^{11} kg of aerosol sulfuric acid (Self et al., 1989; Francis, 1994). Although in Indonesia, effects of Tombora have been reported in eastern North America, Europe and various ice cores invariably show a strong acidity associated with 1815 (Briffa et al., 1998). Although never previously documented in western North America, our tree-ring data does show an association with the Tombora eruption. The magnitude of the emissions estimated from Tombora are huge, as a point of comparison, SO_2 emissions for the entire United States in 1972 (considered the peak) would translate to ca. 1.5×10^{11} kg sulfuric acid, less than the estimate for the Tombora eruption of 1815. We postulate that the Tombora eruption and associated acid rain decreased soil pH increasing selective element solubility and plant uptake creating higher element distribution patterns in the tree. During a La Nina year a vigorous sub-tropical jet stream moves northeastward across the Pacific, the moisture originates near the Philippines and Indonesia. The warm, humid air typically makes its landfall in the Northwest (e.g. Washington, USA) and often merging with big North Pacific storms to produce the area's biggest rainstorms. Since then, the lack of acid rain has resulted in elements that are eventually less and less available to the trees causing a steady decline of these elements in the tree.

Jonsson's et al. (1997) tree-ring data shows a constant, gradual increase in Cd concentrations from 3 ppb in the 1840s to 14 ppb in the 1990s, in a study area near local sources of Cd and Zn emitting industries (Jonsson et al., 1997). Although global atmospheric emissions of Pb, Zn, and Cu have continued to increase in the last century (Nriagu, 1996), tree concentrations of heavy metals, in the study reported here have decreased during the last century. Without direct local sources as in the Jonsson's studies, the global atmospheric load has not affected tree-ring cadmium. Cadmium is at a historically low concentration within the tree-rings in this study.

Tree concentrations of cations have been reported to be decreasing this century in some regions of eastern North America: Ca has decreased by 60% (Bondietti et al., 1990), Mg by 29% (Bondietti et al., 1990), and Zn by 30% (Sheppard and William, 1975; Hasanen and Huttunen, 1989). Bondietti et al. (1990) infers that changes in concentration trends of Ca^{2+} and Mg^{2+} in red spruce trees are a result of regional (eastern North America, USA) mobilization of cations in the rooting zone from extended exposure to anthropogenic acid rain (mid 1900s). In our samples, the cations, barium and strontium, have decreased over the last 150 years by 60% and 45% respectively. Our data indicate zinc has also decreased over the last 150 years about 70% (see Fig. 4). Because we have a longer time record of data, interesting barium, strontium, cadmium and zinc have been declining for over 100 years. Anthropogenic acid rain cannot account for our observed cations trend. We however, postulate that it may be the lack of natural volcanic acid rain that has minimized element mobility in this region.

Copper shows a small cyclic pattern of increasing and decreasing tree concentrations between 1678 and the late 1800s; Cu concentrations cycle between 0.3 and 0.6 ppm. Throughout the 1900s, Cu concentrations are relatively constant at 0.3 ppm. The cyclic concentration patterns are closely associated with several local fire dates; Cu concentrations increase for years near a fire date and then slowly decline following the fire date. In tree-ring data from the Hall et al. (1990) study, high concentrations of Cu in tree-rings were also correlated with fire dates. Although fire does increase bioavailability of many nutrients and trace micro-nutrients, fire does not release all elements from the soil/forest litter equally. For example, after a fire the subsequent uptake of nutrients and micro-nutrients in wheat plants showed that some elements increase while others decrease. This phenomenon is due to some antagonistic soil bioavailable chemistries. Bioavailable zinc is strongly affected by pH, while copper is little affected by pH (Sillanpaa, 1982). When a fire occurs it does breakdown plant material; however, fire is known to also increase the pH of soil (Kutiel and Shaviv, 1993). Therefore, while zinc may be "initially released" the pH increase from the fire has an antagonistic effect by making zinc less plant bioavailable due to increases in soil pH. Therefore, zinc in the tree does not display any changes due to fire events. However, copper is made bioavailable from fire and does not have much of a pH effect that probably accounts for the increase in tree-ring copper associated with fire dates while none is observed for zinc. In this study, Cu concentrations decrease to a historical low of 0.1 ppm from 1800 to 1810, which is just prior to the 1815 volcanic eruption of Tambora, Indonesia. There is a small trend of increasing copper

post 1815, this small increase can be explained by the lack of a strong pH effect for copper plant bioavailability.

8. Conclusions

The largest temporal difference in element concentrations in the tree-rings of the ponderosa pine cannot be correlated with any known local events. Small temporal differences for some elements (copper) can be associated with several local fire events. The largest temporal differences in element tree-ring concentrations can be associated to global environmental changes, specifically volcanic eruptions. Unlike many tree-ring studies, our trend of declining element concentrations occurs for 150 years and cannot be explained by exposure to anthropogenic acid rain, as our study site is not exposed to recent acid rain. The digestion and ICP-MS analyses method described is fast, robust, and is not labor intensive, as well, reagents and the waste stream are minimized.

Acknowledgements

We would like to thank B. Loper, E. Johnson, A. Ungerer, B. Haley, Drs. A. Azarenko, J. Jenkins, and W. Crannell from Oregon State University, and L. Shaw and staff in the Wenatchee National Forest. K.P. would also like to acknowledge the D.B. DeLoach Research Scholarship from Oregon State University for partially funding of this project.

References

- Acidification in Finland, 1987. Ministry of Environment and Ministry of Agriculture and Forest, Finnish Research Project on Acidification (HAPRO) Secretariat, Helsinki.
- Anderson, K.A., 1996. Micro-digestion and ICP-AES analysis for the determination of macro and micro elements in plant tissues. *Atomic Spectrosc.*, 30–33.
- Baes, C.F., McLaughlin, S.B., 1984. Trace elements in tree-rings: Evidence of recent and historical air pollutants. *Science* 224, 495–496.
- Bondiatti, E.A., Momoshima, N., Shortle, W.C., Smith, K.T., 1990. A Historical perspective on divalent cation trends in red spruce stemwood and hypothetical relationship to acidic deposition. *Can. J. For. Res.* 20, 1850–1858.
- Briffa, K.R., Jones, P.D., Schweingruber, F.H., Osborn, T.J., 1998. Influence of volcanic eruptions on northern hemisphere summer temperatures over the last 600 years. *Nature* 393, 450–455.
- Bukovac, M.J., Wittwer, S.H., 1957. Absorption and mobility of foliar applied nutrients. *Plant Physiol.* 32, 428–435.
- Carlquist, S., 1988. *Comparative Wood Anatomy*. Springer Verlag, New York.
- Cutter, B., Guyette, R., 1993. Anatomical, chemical and ecological factor affecting tree species choice in dendrochemistry studies. *J. Environ. Qual.* 22, 611–619.
- Francis, P., 1994. *Volcanoes a Planetary Perspective*. Oxford University Press, New York, p. 443.
- Gartner, B.L. (Ed.), 1995. *Plant Stems: Physiology and Function Morphology*. Academic Press Inc., San Diego, pp. 343–357.
- Gerloff, G.C., Moore, D.G., Curtis, J.T., 1996. Selective absorption of mineral elements by native plants of Wisconsin. *Plant Soil.* 25, 393–405.
- Gilfrich, J.V., Gilfrich, N.L., Skelton, E.F., Kirkland, J.P., Qadri, S.B., Nagel, D.L., 1991. *X-Ray Spectrom.* 20, 203–208.
- Hall, G.E.M., Pelchat, J.-C., 1990. Analysis of standard reference materials for Zr, Nb, Hf, Ta by ICP-MS after lithium metaborate fusion and cupferron separation. *Geo-stands Newslett.* 14/1, 197–206.
- Hall, G.S., Yamaguchi, D.K., Rettberg, T.M., 1990. Multielemental analyses of tree-rings by inductively coupled plasma mass spectrometry. *J. Radional. Nucl. Chem.* 146/4, 255–265.
- Hasanen, E., Huttunen, S., 1989. Acid deposition and the composition of pine tree-rings. *Chemosphere* 18 (9/10), 1913–1920.
- Hagemeyer, J., 1993. *Plants as Biomonitors: Indicators for Heavy Metals in the Terrestrial Environment*. Bernd Markert, New York, pp. 541–563.
- Hagemyer, J., Weinand, T., 1995. Radial distribution patterns of Pb in stems of young Norway spruce trees grown in Pb-contaminated soil. *Tree Physiol.* 6, 591–594.
- Hedin, L.O., Likens, G.E., 1999. Atmospheric dust and acid rain. *Sci. Amer.*, 70–74.
- Holtzman, R.B., 1970. Isotopic composition as a natural tracer of lead in the environment. *Environ. Sci. Technol.* 4, 314–317.
- Jonsson, A., Eklund, M., Hakansson, K., 1997. Heavy metals in the environment. *J. Environ. Qual.* 26, 1638–1643.
- Kutieli, P., Shaviv, A., 1993. Effects of soil type, plant composition, and leaching on soil nutrients following a simulated forest fire. *Forest Ecol. Manage.* 53, 329–343.
- Lepp, N.W., 1975. The potential of tree-ring analysis for monitoring heavy metal pollution patterns. *Environ. Pollut.* 9, 49–61.
- Lukaszewski, Z., Siwecki, R., Opydo, J., Zembrzudki, W., 1988. *Trees* 2, 1–6.
- Matusiewicz, H., Barnes, R.M., 1985. Tree-ring wood analysis after hydrogen peroxide pressure decomposition with inductively coupled plasma atomic emission spectrometry and electrothermal vaporization. *Anal. Chem.* 57, 406–411.
- Meisch, H.U., 1986. Distribution of metals in annual rings of the beech (*Fagus sylvatica*) as an expression of environmental changes. *Experientia* 42, 537–542.
- Momoshima, N., Bondiatti, E.A., 1994. The radial distribution of Sr 90 and Cs 137 in tress. *J. Environ. Radioactivity* 22/2, 93–109.
- Narcisco, C., 2000. Personal communication. Okanogan-Wenatchee National Forest Geologist/Geomorphologist. cnarcisco@fs.fed.us, 8 August.

- Nriagu, J.O., 1996. History of global metal pollution. *Science* 272, 223–224.
- Partridge, M., 1999. Immense, ancient pine tree that fell in March offers look into past. *The Oregonian* [Portland]. 10 August B02.
- Prohaska, T., Stadlbauer, C., Winner, R., Stingeder, B., Latkoczy, Ch., Hoffmann, E., Stephanowitz, H., 1998. Investigation of element variability in tree-rings of young Norway spruce by laser-ablation-ICPMS. *Sci. Total Environ.* 219, 29–39.
- Queirolo, F., Valenta, P., Stegen, S., Breckle, S.W., 1990. Heavy metal concentrations in oak wood growth rings from the Taunus (Federal Republic of Germany) and the Valdivia (Chile) regions. *Trees* 4, 81–87.
- Ragsdale, H.L., Berish, C.W., 1988. The decline of lead in tree-rings of *Carya* spp. In urban Atlanta, GA, USA. *Biogeochem.* 6, 21–29.
- Robitaille, G., 1981. Heavy-metal accumulation in the annual rings of balsam fir *Abies Balsamea* (L) mill. *Environ. Pollut. Ser. B* 2, 193–202.
- Ross, S., 1994. Toxic metals in soil plant systems. Wiley, New York.
- Schutt, P., 1989. Symptoms as Bioindicators of Decline in European Forests. *Biologic Markers of Air-Pollution Stress and Damage in Forests*. National Academy Press, Washington, DC, pp. 119–123.
- Self, S., Rampino, M.R., Newton, M.S., Wolff, J.A., 1989. Volcanological study of the great tumbora eruption of 1815. *Geology* 12, 659–663.
- Shaw, L., 2001. Personal communication. Okanogan-Wenatchee National Forest Reforestation Specialist. Lshaw@fs.fed.us, 5 June.
- Sheppard, J.C., William, H.F., 1975. Trees as environmental sensors monitoring long-term heavy metal contamination of spokane river, Idaho. *Environ. Sci. Technol.* 9/7, 638–642.
- Siau, J.F., 1970. Pressure impregnation of refractory hardwoods. *Wood Sci.* 3, 1–7.
- Sillanpaa, M., 1982. Micronutrients and the nutrient status of soils. A Global Study. UN Food and Agriculture Organization, Rome, Italy.
- Smith, K.T., Shortle, W.C., 1996. Tree biology and dendrochemistry. In: Dean, J.S., Meko, D.M., Swetnam, T.W. (Eds.), *Tree-rings Environment and Humanity*. Radiocarbon, Tucson, pp. 629–635.
- Stark, N., Essig, D., Baker, S., 1989. Nutrient concentrations in *Pinus ponderosa* and *Pseudotsuga menziesii* xylem sap from acid and alkaline soils. *Soil Sci.* 148, 124–131.
- Suzuki, T., 1975. The tree width and the contents of Cd, Zn and Pb in wood annual rings of the Sugi tree growing in an area contaminated by Cd from a zinc refinery at Annaka, Gunma. *J. Jap. For. Soc.* 57, 45–52.
- Tyler, G., Berggren, D., Bergkvist, B., 1987. Soil acidification and metal solubility in forests of south Sweden. In: Hutchinson, T.C., Meema, K. (Eds.), *Effects of Atmospheric Pollutants on Forests, Wetlands, and Agricultural Ecosystems*. Springer Verlag, New York.
- U.S. Geological Survey, 2001. <http://water.usgs.gov/nwc/NWC/pH/html/ph.html>.
- Valkovic, V., Rendic, D., Biegert, E.K., Andrade, E., 1979. Trace element concentrations in tree-rings as indicators of environmental pollution. *Environ. Int.* 2, 27–32.
- Zimmermann, M.H., Grown, C.L., 1971. *Trees, Structure and Function*. Springer Verlag, Berlin.