HIGH-RESOLUTION DENDROCHEMICAL ANALYSIS OF FLOOD-AFFECTED OAKS USING LASER ABLATION ICP-MASS SPECTROMETRY

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SUMMARY

Dendrochemical analysis was conducted on Quercus macrocarpa Michx. (bur oak) growing within the floodplain of the Red River, Canada, to determine if xylem formed during severe floods contained significantly perturbed chemistry. Wood samples were taken from five living trees in the same stand and from three timbers from a 19th-century building. Laser ablation ICP-mass spectrometry was used to determine the trace element chemistry in the earlywood and latewood of rings formed before, during and after major floods. Between-tree correlations were significant (p < 0.05) for Hg, Mg, Mn, Sr and Zn, suggesting that changes in the abundance of these elements over time might reflect common physiological processes or environmental signals. Mg, Mn and Sr concentrations were higher in the earlywood than in the latewood for both living and historical samples. These intra-annual shifts may reflect varying rates of uptake driven by seasonal changes in anatomical development, as well as stability of these elements after their initial deposition. Although no chemical anomalies are associated with 20th-century floods, earlywood coinciding with an extreme flood in 1826 contained low levels of Mg, Mn and Sr. These elemental anomalies might represent an independent biochemical flood signature but it is also possible they are a secondary expression of wood formation disrupted by flooding. In either case, elemental analysis does not provide any information beyond that obtained from studying anatomical features, and does not appear to be a viable tool to identify the occurrence of past floods.

Key words: Dendrochemistry, floods, tree rings, Red River, laser ablation ICP-MS.

INTRODUCTION

Dendrochemical analysis measures the level of nutrients and trace elements in stemwood to determine past changes in uptake and translocation (Lewis 1995), which are commonly interpreted to reflect macroenvironmental trends. Most research using chemical

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records derived from tree rings has focused on estimating the historical abundance of environmental pollutants. Studies have identified common trends between elemental concentrations in tree rings and air pollution from power plants (Pärn 2001), battery plants (Eklund 1995), smelters (Symeonides 1979; Watmough & Hutchinson 1996) and large-scale emissions from diffuse sources (Jonsson et al. 1997). Dendrochemistry has also been used to document hydrological changes in wetlands, including influences from salt-solution mining (Yanosky & Kappel 1997) and saltwater flooding in estuaries (Yanosky et al. 1995), as well as groundwater contamination (Vroblesky & Yanosky 1990; Yanosky & Vroblesky 1992). Most dendrochemical studies have documented long-term changes in environmental conditions occurring over several decades using aggregate measurements from several rings (commonly combining 5, 10 or 20 rings; e.g., Guyette & Cutter 1994; Schaumlöffel et al. 1998; Pärn 2001) or by measuring the chemistry of non-consecutive rings (e.g., McClenahen et al. 1989; Vroblesky & Yanosky 1990; Yanosky et al. 1995). However, it is possible that high-resolution analysis of tree chemistry could be used to identify perturbations caused by environmental events that occur at shorter timescales.

Spring flooding is known to cause rapid changes in soil chemistry, most commonly by affecting the abundance of certain mineral elements and creating prolonged hypoxic or anoxic conditions (Marschner 1986). Because flood-induced changes to soil conditions can affect root respiration and ion absorption, dendrochemical records from flooded trees may include evidence of elemental ‘shocks’ caused by past flooding. Flooding can exert significant effects on plant nutrition and elemental chemistry through concomitant changes in soil chemistry, plant nutrient absorption, and other physiological processes (Kozlowski & Pallardy 1984). Several studies have demonstrated that extreme flooding during the growing season may cause oak trees to develop unusual anatomical features. In seedlings of bur oak (Quercus macrocarpa Michx.), flooding induces hypertrophied lenticels and adventitious roots to form along the submerged portion of the stem (Tang & Kozlowski 1982). Flooding of mature oaks leads to the development of anomalously small vessels in their earlywood; in extreme cases, these trees may also display disorganised latewood and thin-walled fibers (Astrade & Bégin 1997; St. George & Nielsen 2003). These anatomical changes might be caused by disruptions of the normal basipetal flow of auxin (Aloni 1991), although the specific mechanism that affects hormonal transport is unknown.

We hypothesised that prolonged inundation might cause riparian trees to develop significantly perturbed wood chemistry. Unequivocal chemical markers could serve as proxy records of severe floods that occurred prior to human observation and provide independent confirmation of paleoflood records derived using traditional tree-ring evidence such as anomalous anatomical structures (e.g. St. George & Nielsen 2003) or impact scars (e.g. McCord 1996). Here we report on the elemental analysis of bur oak xylem formed during several severe floods in the Red River valley, Manitoba, Canada. Because Mn and Fe are used by soil microorganisms as alternative electron acceptors in respiration under anoxic conditions (Marschner 1986), we speculated that higher concentrations of these elements might be present within wood formed during major spring floods. To obtain data that would allow us to investigate the potential of flooding
to induce annual or subannual changes in wood chemistry, laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) was employed to determine elemental concentrations within individual tree rings. LA-ICP-MS has previously been used in only a few dendrochemical pollution studies (e.g. Watmough et al. 1998); the present study is the first application of the method to trees growing under nonpolluted soil conditions. We discuss seasonal changes in tree-ring chemistry that may be related to changes in elemental uptake during the growth year, and evaluate elemental anomalies that are associated with extreme flooding.

MATERIALS AND METHODS

Wood samples

Tree-ring samples were taken from bur oak that had grown within the riparian forest surrounding the Red River in Manitoba, Canada, including both living trees and timbers from a mid-19th century building. In general, white oak species such as bur oak have a number of habit- and xylem-based factors that are considered beneficial for dendrochemical analysis (Cutter & Guyette 1993). The live trees were growing approximately 350 meters west of the Red River, near the USA-Canada border (49°01' 50" N, 97° 12' 10" W). These oaks were cored in the autumn of 1998 and were mature trees ranging between 117 and 133 years old. Hydrographs indicate that several large floods affected this stand during the 20th century, with the trees inundated for 24 days in 1979, 30 days in 1997 and 40 days in 1950. Although other oaks at this site collected in 2001 did contain flood signatures for the 1997 and 1950 floods (St. George et al. 2002), the trees used in this study did not contain any obvious anatomical anomalies associated with these or any other floods. The historic timbers were salvaged from Barber House, a mid-19th century building in Winnipeg, and had been cut from trees that grew between 1655 and 1863. Although the growth location of these trees is unknown, the distribution of oaks in the Red River valley, as well as contemporary woodcutting practices, suggest that these trees were probably harvested within 100–200 meters of the Red River in the vicinity of central Winnipeg. All timber samples from Barber House contained anatomical signatures associated with Red River floods in 1826 and 1852, including atypically small earlywood vessels, disorganised flame parenchyma and thin-walled fibres (St. George & Nielsen 2000). The dating of each growth ring was confirmed by comparing the ringwidth pattern of each specimen against a regional master chronology derived from more than 400 oaks (St. George & Nielsen 2003).

Dendrochemical measurements were obtained from rings formed during 20–50-yr periods surrounding major 19th and 20th century floods. Data obtained from live trees spanned, at minimum, the period 1976–1998, while those from the historical timbers had a common period of 1816–1828.

LA-ICP-MS

Elemental analyses were carried out using an Elan 6100 ICP-mass spectrometer (Perkin-Elmer – Sciex, Concord, Ontario) linked to an ultraviolet wavelength laser ablation unit (LUV266, New Wave Products, Warwick, Rhode Island, U.S.A.). Oak cores
were cut into smaller sections to fit inside the 6-cm diameter sampling cell. Ablated material was transported to the ICP nebulizer inlet along Tygon tubing by Ar gas flowing at 0.9 L/min. Each ring was ablated with two parallel transects through the earlywood and latewood; the laser control software allowed the shape of the transect to be altered as necessary to remain within the wood type of interest.

Laser operating conditions were optimised to give the highest and most stable signals possible. The conditions included: a laser beam diameter of 100 μm (giving an effective sampling area 130 μm wide); a 10 Hz pulse firing at 1.8 mJ per pulse; and a 50 μm/s sampling transit. The laser was warmed up at the start of each day by firing at a neutral target for 10 min, and was allowed to fire without ablation for 3 s prior to each ablation. Each ablation event lasted 50 s, giving a total raster on the sample surface of 2.5 mm. A few rings were too narrow to sample using a 100 μm beam size; in these cases, the beam was reduced to 40 μm (producing an ablation trench 60 μm wide). The differences in element intensities caused by different beam diameters were corrected by normalising element data against $^{13}$C, which represents the amount of matrix (wood) ablated from the sample.

The ICP-MS operating conditions (lens voltage, nebulizer gas flow, torch position, plasma power) were optimised through ablation of an in-house standard wood material. This standard was prepared by sectioning a 3 × 3 cm block of pine wood at an angle perpendicular to its rings, thereby exposing a wood surface from a single ring. Pine is preferable to deciduous species for this purpose due to the lack of distinct early- and latewood bands within its annual rings. This wood standard was also ablated regularly throughout the experimental work to characterise analytical precision.

Signal intensity data were collected for the following elements using the isotopes indicated: $^{13}$C, $^{25}$Mg, $^{55}$Mn, $^{57}$Fe, $^{59}$Co, $^{60}$Ni, $^{63}$Cu, $^{66}$Zn, $^{86}$Sr, $^{98}$Mo, $^{107}$Ag, $^{114}$Cd, $^{138}$Ba, $^{139}$La, $^{202}$Hg, $^{208}$Pb and $^{238}$U. Data were acquired in peak hopping mode, with a dwell time of 50 ms. The gas blank of the instrument was established during the 5 s period immediately prior to laser firing. Signal data were processed off-line using the Glitter software package (GEOMOC, Macquarie University, Sydney, Australia). The average blank signals were automatically subtracted from the signals acquired while the laser was firing, and a time-integrated average intensity for each element was calculated for each sample. The $^{13}$C intensity was used to normalise all other element intensities to account for slight variations in the ablated mass between samples. Periodic sampling of the in-house wood standard allowed for variations due to instrument sensitivity drift to be corrected. Typically, a mean was calculated from four replicate analyses of the standard conducted about every two hours. Sample data were then adjusted using this mean as the baseline.

The element data were not converted to concentrations due to the lack of certified wood standard reference materials (SRMs) or calibration standards. The lack of suitable (matrix-matched) solid SRMs and calibration standards is a long-standing problem in the application of LA-ICP-MS to the environmental/biological sciences (Outridge et al. 1995), and many recent studies (e.g. Lee et al. 1999; Vander Putten et al. 2000) have similarly used only matrix element-normalisation of data. Watmough et al. (1998) developed their own series of calibration standards using wood taken from trees along
a 40-km transect away from a polluted site and demonstrated that signal intensity with a UV laser system was linear to concentrations in the wood for seven elements over the ICP-MS’ working range (which spans several orders of magnitude). Fortunately, concentration data were not critical for this study because our objectives focused on the relative elemental differences between early- and latewood, between rings, between trees, and the correspondence between unusual element content and known floods.

Statistical analysis
Elemental concentrations for living and historical tree-ring samples were averaged to develop composite or summary series for each group. Prior to averaging, data from each tree were converted into deviates with respect to mean abundance within the heartwood so that each tree made an equal contribution to the composite series. Sapwood rings were not used to calculate mean abundance, because, for several elements (particularly Mn and Mg), the outermost four to ten rings contained concentrations that were one to two orders of magnitude greater than those in the heartwood. Calculating deviates from average values over the entire tree would have caused all measurements from heartwood rings to report as negative values.

RESULTS
Analytical precision
Repeated analysis of the in-house wood standard over the course of the experiment showed that analytical precision varied from 5.7% relative standard deviation (RSD) for Mn to 56% for Co (Table 1). The differences in measurement precision between elements cannot be attributed solely to differences in signal intensities. For example, while Sr had a $^{13}$C-normalised intensity of about 0.015 and that of Mn was $>8$, both displayed a similarly low level of variation (7.1 and 5.7% RSD, respectively). Conversely, elements such as Fe and Pb had several times higher signal intensities than Sr but exhibited much greater levels of analytical imprecision. These patterns imply that some elements were distributed much more homogeneously within the wood standard than others, even though the standard consisted of wood from within a single tree ring.

Elements showing common trends between trees
Any potential chemical signal caused by a stand-wide exogenous disturbance should be present in most trees within that stand, as elemental trends that vary greatly from one tree to the next would not constitute credible evidence of past environmental forcings. Several elements do follow similar temporal trends in trees from both the living and historical sample sets. During the common intervals for the two groups of trees (1976–1998 and 1816–1828), average between-tree correlations were significant ($p < 0.05$) for Hg, Mg, Mn, Sr and Zn (Table 2). Although significant correlations were also found for Ag, Cu and Pb in the historical timbers, these elements were not correlated in the living trees. The shared trends between trees suggest that variations in Hg, Mg, Mn, Sr and Zn are related to factors common to all trees and could potentially reflect changes in local environmental conditions. The remaining elemental series are unlikely to reflect historical changes in macro-scale environmental abundance faithfully.
Table 1 – Analytical precision of LA-ICP-MS determination of elements in an in-house pine wood standard. Mean and standard deviation values for all elements are signal intensities normalised against the signal intensity for $^{13}$C. The mean signal intensity of $^{13}$C (integrated over the entire sampling raster for each wood layer) is given as counts per second.

<table>
<thead>
<tr>
<th>Element</th>
<th>Mean</th>
<th>SD</th>
<th>RSD</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>120,300</td>
<td>53700</td>
<td>44.6</td>
</tr>
<tr>
<td>Mg</td>
<td>0.168</td>
<td>0.011</td>
<td>6.4</td>
</tr>
<tr>
<td>Mn</td>
<td>8.405</td>
<td>0.479</td>
<td>5.7</td>
</tr>
<tr>
<td>Fe</td>
<td>0.057</td>
<td>0.020</td>
<td>34.8</td>
</tr>
<tr>
<td>Co</td>
<td>0.002</td>
<td>0.001</td>
<td>55.7</td>
</tr>
<tr>
<td>Ni</td>
<td>0.006</td>
<td>0.002</td>
<td>34.4</td>
</tr>
<tr>
<td>Cu</td>
<td>0.084</td>
<td>0.024</td>
<td>27.9</td>
</tr>
<tr>
<td>Zn</td>
<td>0.16</td>
<td>0.030</td>
<td>18.8</td>
</tr>
<tr>
<td>Sr</td>
<td>0.015</td>
<td>0.001</td>
<td>7.1</td>
</tr>
<tr>
<td>Mo</td>
<td>0.0004</td>
<td>0.0002</td>
<td>39.4</td>
</tr>
<tr>
<td>Ag</td>
<td>0.004</td>
<td>0.001</td>
<td>18.2</td>
</tr>
<tr>
<td>Cd</td>
<td>0.003</td>
<td>0.001</td>
<td>26.9</td>
</tr>
<tr>
<td>Ba</td>
<td>0.801</td>
<td>0.093</td>
<td>11.7</td>
</tr>
<tr>
<td>La</td>
<td>0.005</td>
<td>0.003</td>
<td>49.2</td>
</tr>
<tr>
<td>Ce</td>
<td>0.006</td>
<td>0.003</td>
<td>52</td>
</tr>
<tr>
<td>Nd</td>
<td>0.002</td>
<td>0.001</td>
<td>56.9</td>
</tr>
<tr>
<td>Hg</td>
<td>0.0007</td>
<td>0.0003</td>
<td>45.3</td>
</tr>
<tr>
<td>Pb</td>
<td>0.075</td>
<td>0.017</td>
<td>23</td>
</tr>
<tr>
<td>U</td>
<td>0.00006</td>
<td>0.00002</td>
<td>37.1</td>
</tr>
</tbody>
</table>

Table 2. Mean between-tree correlations for individual elements.

<table>
<thead>
<tr>
<th>Element</th>
<th>$r^a$</th>
<th>$r^b$</th>
<th>$r^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>0.03</td>
<td>0.43**</td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.08</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.01</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>0.18</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.15</td>
<td>0.33*</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.15</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.34**</td>
<td>0.42*</td>
<td></td>
</tr>
<tr>
<td>La</td>
<td>0.07</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>0.65**</td>
<td>0.84**</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.53**</td>
<td>0.87**</td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>0.20</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>0.05</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.05</td>
<td>0.42*</td>
<td></td>
</tr>
<tr>
<td>Sr</td>
<td>0.47**</td>
<td>0.75**</td>
<td></td>
</tr>
<tr>
<td>U</td>
<td>0.18</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.32*</td>
<td>0.61**</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 1. Composite elemental series for Mg, Mn and Sr. Data obtained from individual trees were standardised with respect to mean concentrations within the heartwood and then averaged. Relative concentrations are shown for both earlywood (grey) and latewood (black).

Fig. 2. Composite elemental series for Hg and Zn.
Trends in wood chemistry

The most striking feature in the composites for several elements is the intra-annual fluctuation in abundance (Fig. 1). Earlywood layers within the heartwood contain higher concentrations of Mg, Mn and Sr, although this alternating pattern is more pronounced in the historical timbers than in the living trees. The relative concentrations of Zn and Hg in the earlywood and latewood are more variable but values are usually higher within the earlywood (Fig. 2). As this pattern is less prominent in elements that are more dissimilar from tree to tree, it seems that synchronous intra-annual fluctuations in wood chemistry contribute a considerable portion of the common between-tree variance for these five elements.

The sapwood of both the living and historical samples contained elevated Mg and Mn levels, which spanned nearly 10 years growth in certain trees. The decreased variability of Mg in the living trees between 1984 and 1990 might reflect its diffusion from the sapwood into adjacent rings, leading to elevated levels within the latewood. The outermost rings from the historical samples show a Sr increase that is not found in the sapwood of living trees. The extremely high Zn levels in the 1824 latewood and the 1837 earlywood are only present in one tree and appear to be outliers.

Potential chemical signatures associated with flooding

The living trees do not show any chemical (or anatomical) anomalies associated with Red River floods that occurred during the 20th century. Although Mg and Mn levels in the earlywood formed in 1979 are low, similarly low values are also present in non-flood years. Zinc levels in the 1979 earlywood are high, but are also not unusual. The chemistry of a single live tree was analysed across a pair of short intervals containing earlier flood years (1916 and 1950; not shown) but no large positive or negative departures in wood chemistry were detected for either flood year. Any potential Mn or Mg flood signatures for 1996 or 1997 would be obscured by the extremely high abundance of these elements in the sapwood. While Hg levels in the 1997 earlywood are relatively high, this increase is also present in the earlywood layer formed in 1998. None of the elements with non-significant between-tree correlations have anomalous values that coincide with major floods.

Results from the historic timbers suggest that a chemical signature related to flooding may be present for wood formed in 1826. The 1826 earlywood layers contained very low levels of Mg, Mn and Sr; 1826 had the only negative earlywood values in the composite records for these three elements. However, other years also had low positive values for these elements, particularly 1828. Levels of Mg, Mn and Sr in the earlywood of 1826 and 1828 are not significantly different. Although the 1852 rings are within the heartwood of the historical oaks and thereby outside the influence of sapwood effects, the earlywood layers of these rings do not show unusually low values of Mn, Mg or Sr.
DISCUSSION

Although these results suggest that many elements in bur oak are highly variable from tree-to-tree, selected elements display consistent long- and short-term trends that appear to be related to internal physiological processes and, less definitely, external environmental forcing factors.

Concentrations of Mg, Mn and, to a lesser extent, Sr are much higher in the sapwood than in the heartwood; sapwood/heartwood ratios in the composite series approach 70 and 200 for Mn and Mg, respectively. Similar increases have also been described within the sapwood of *Quercus robur* L. (De Visser 1992) and *Quercus petraea* Liebl. (Masson *et al.* 1997). Elevated Mn and Mg concentrations in the sapwood are believed to reflect the retrieval and recycling of these elements, which are essential for plant growth (Wardell & Hart 1973). Several authors have reported that Mn and Sr concentrations in trees can be affected by changing environmental conditions, including soil acidification (Lévy *et al.* 1996) and liming (McClonahen *et al.* 1989; Kashuba-Hockenberry & DeWalle 1993), but there is no evidence that such changes have occurred in the Red River valley.

Relatively little previous work has documented differences in elemental concentrations between earlywood and latewood layers. Although Hall and Nauman (1984) reported a tendency for higher elemental concentrations in earlywood than in latewood of pitch pine (*Pinus rigida* Mill.), Yanosky and Vroblesky (1992) did not find any consistent differences in nickel concentrations between the earlywood and latewood in *Quercus falcata* Michx. growing on a contaminated aquifer. Similarly, McClonahen *et al.* (1989) reported no significant differences between earlywood and latewood chemistry for 11 elements, including Mg, Mn and Sr, in *Liriodendron tulipifera* L. Our analysis has shown that Mg, Mn and Sr series in bur oak contain a strong intra-annual structure, where concentrations are consistently higher in the earlywood than in the latewood.

These intra-annual patterns may indicate that radial translocation of these elements, which is the primary confounding factor in dendrochemistry, is relatively minor. Many elements in trees are translocated from the xylem toward the centre of the stem to dispose of waste material and outwardly to satisfy the metabolic requirements of the cambium (Stewart 1966). This transfer influences the radial distribution patterns of elements, as elements that are incorporated into the current year’s ring can be transported into prior or subsequently-formed rings (Hagemeyer 1993). This process can potentially violate the assumption that the element concentrations in a given growth ring reflect environmental conditions at the time of wood formation (Guyette *et al.* 1992) and invalidate the use of dendrochemistry for historical biomonitoring purposes (Hagemeyer 1993).

The occurrence of elemental translocation is difficult to either prove or disprove convincingly, largely because it is a gradual process that occurs over the lifespan of the tree. Ideally, the long-term influence of translocation on dendrochemical series would be determined with sampling or monitoring programs conducted over several decades. This approach has rarely been adopted in dendrochemical studies (however, see McClonahen *et al.* 1989), which instead have attempted to establish temporal stability by linking trends in dendrochemical series with historical patterns of elemental avail-
ability. Translocation is also assumed to be minimal if large abrupt gradients in concentration are not detected at the heartwood-sapwood boundary (Yanosky et al. 1995) or if elemental trends correspond closely with assumed environmental forcings (e.g., Symeonides 1979; Eklund 1995). Additionally, since translocation should lead to smoothed distribution patterns for affected elements (Gilboy et al. 1979), high interannual variability within the tree has been interpreted to indicate that elements have not been mobile since the formation of the growth ring (Hoffman et al. 1996).

Our results could be interpreted as evidence that Mg, Mn and Sr are not mobile after they are incorporated into the woody tissue of bur oak. If these elements are relatively stable after their initial uptake and deposition, the observed shifts in earlywood-latewood chemistry would reflect varying rates of uptake in spring and summer driven by seasonal changes in anatomical development. The vascular system is one of the three main pathways of elemental uptake in trees, as elements are moved from the soil via the roots and are subsequently transported into the xylem (Lepp 1975). Because Mg, Mn and Sr levels in the earlywood are consistently high, the vascular system of bur oak may become enriched in these elements while serving as part of the tree’s active conductive system. However, it is also possible that elevated Mg, Mn and Sr levels in the earlywood might indicate either their preferential deposition during heartwood formation or their retention during removal or recycling. Under that scenario, earlywood/latewood shifts in elemental concentrations would reflect varying storage capacities rather than increased seasonal uptake. Our data does not allow us to determine which of these two competing interpretations is correct.

Is the xylem chemistry of bur oak perturbed significantly by large floods? Earlywood formed during extreme Red River floods does contain anomalously low levels of Mg, Mn and Sr. This observation contradicts our initial hypothesis that xylem formed during floods should have elevated levels of Mn and Mg, and implies that the increased availability of these elements in the environment does not necessarily lead to higher concentrations in woody tissue. Historical and dendrochronological evidence suggests that the 1826 flood was the most severe since at least A.D. 1648 (St. George & Nielsen 2003). This flood is the only event associated with decreased Mn, Mg and Sr concentrations, and it is possible that only the very largest and/or long-lasting floods can stimulate a biochemical response in riparian trees. Lesser floods, like those experienced in 1950 and 1979, may not have inundated trees to a sufficient depth and/or duration to produce a chemical tree-ring signature. However, it is also possible that these chemical changes may be a secondary effect of anatomical abnormalities caused by flooding, rather than an independent flood signature. All three tree-ring samples derived from historical timbers contained anatomical flood signatures in 1826. Since these signatures are identified primarily by their small earlywood vessels, their earlywood layers are deficient in the major anatomical structures that distinguish them from latewood. If the earlywood vessels or tyloses are the major store of Mg, Mn and Sr within the annual rings of bur oak, the abnormal structure of flood rings would account for their lowered elemental concentrations relative to normal rings. Any variation in the relative proportion of cell types over time might therefore cause tree-ring chemical series to reflect these anatomical changes and mask any environmental signals. The sampling approach used in
this study does not allow us to identify the relative contribution of each cell type to the mean chemistry of each earlywood and latewood layer. However, if chemical composition in oak does vary by cell type, the apparent Mg, Mn and Sr signatures present in 1826 would simply represent the elemental expression of a disrupted wood anatomy. In that case, the relative complexity of the anatomy of ring-porous trees may represent an additional complicating factor that should be considered in future dendrochemical studies.

Regardless of their root cause, it seems clear that these elemental anomalies in bur oak tree rings provide limited information about the occurrence of past floods. Unusually low concentrations of Mg, Mn and Sr within the earlywood have been observed only within rings that also contain anatomical abnormalities caused by flooding; therefore elemental data does not provide any additional information beyond that obtained from the study of anatomical features. Despite its relative speed and ease-of-use compared to other dendrochemical analyses, the laser ablation method is still slower and more expensive than simple visual inspection of tree-ring anatomy. For these reasons, we conclude that dendrochemical analysis of bur oak is not a viable tool to identify floods that took place prior to direct observation.

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REFERENCES


