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SOME CONSIDERATIONS IN THE RECONSTRUCTION OF LEAD LEVELS USING LASER ABLATION: LESSONS FROM THE DESIGN STAGE OF AN URBAN DENDROCHEMISTRY STUDY, ST. JOHN'S, CANADA

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Abstract: Study of soils in St. John's, Canada showed elevated Pb levels representing a potential exposure risk for young children. Old trees growing in the city present a potential annually-resolved record of Pb levels over past centuries that provides important temporal and spatial dimensions to Pb exposure risk assessment. This paper reports the results of our analytical tests to develop a fast, reliable and cost-efficient method using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for measuring Pb concentration in annual tree rings from available tree species. Our tests focused on approaches to sample preparation as they affect the laser ablation process, the relative merits of the ablation sampling method, and the response of our available tree species, which have contrasting wood structures, to laser ablation. The range of annual Pb concentrations (ppm) measured for each of the study species were as follows: spruce (0.18–6.42); elm (0.12–7.91); and horse chestnut (0.40–14.09). Our results demonstrate that the cutting procedure for preparing tree cores produced the most consistent Pb concentrations of the three methods, although they each displayed problematic anomalies. The selection of the best laser ablation technique appears to be highly dependent on study species and goals. In general, spot analysis permits detailed and targeted studies of tree-ring structures, but requires careful sampling attention for species with complex wood anatomy. The line scan method is ideal for reconstructing annually resolved element concentrations from trees and to some degree mitigates the complicating issue of intra-ring variability. Horse chestnut was determined to be the best of the available tree species because it exhibited a good response to laser ablation and produced the lowest intra-ring variations in Pb concentration.

Keywords: tree rings, dendrochemistry, laser ablation, ICP-MS, urban lead contamination.

1. INTRODUCTION

The most widely used proxy data that provide information on historical pollution are derived from ice cores, peat bogs and lake sediments (e.g. Graney *et al.*, 1995; Shotyk *et al.*, 1996 and Osterberg *et al.*, 2008), even though their spatial resolution is limited. Trees are another source of long-term data on pollution (e.g. Stravinskiene *et al.,* 2013, Malik *et al.,* 2012). Annual growth rings of trees have the potential to record and preserve annually resolved metal concentrations from atmospheric and soil sources, a technique known as dendrochemistry (Watmough, 1999, McLaughlin *et al.,* 2002). The advantage of the dendrochemical approach is the wide geo-

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graphical distribution of trees providing an abundance of study material, easy accessibility, low cost of sample collection and high spatial resolution. The main advantage in comparison with ice cores and varves is the fact that for trees in temperate latitudes usually one tree ring represents one year that can be easily assigned a calendar date.

Trees are not a passive recorder of environmental changes and many processes involved in the uptake, transportation and deposition of heavy metals within trees have to be considered during the various stages of dendrochemical analysis (Lepp, 1975 and Smith and Shortle, 1996). For example, the radial translocation of elements across tree rings can compromise the temporal resolution of the technique (Cutter and Guyette, 1993). There are many factors involved in determining the suitability of particular species or an individual tree for dendrochemical study (Cutter and Guyette, 1993). Habitat-based factors are connected with local site characteristics where tree species grow and include for example microclimate, soil, slope, and aspect. Xylem-based factors represent anatomical, chemical and physical characteristics of tree species that control wood permeability and fluid flow. Finally, element-based factors such as chemistry regulate element mobility in tree species. The choice of a study species therefore should take into consideration the particular biogeographical setting, chemical properties of the element in question, and study aims (Cutter and Guyette, 1993). Many of the challenges encountered in dendrochemical studies can be overcome by selection of appropriate species, sampling strategies and analytical methods (Cutter and Guyette, 1993; Watmough *et al.*, 1998a and Watmough, 1999).

The most popular methods for chemical analysis of wood — inductively coupled plasma mass spectrometry (ICP-MS) and atomic emission spectroscopy (ICP-AES) — are based on element detection from digested wood (e.g. Aznar *et al.*, 2008; Kirchner *et al.*, 2008; Lageard *et al.*, 2008; Saint-Laurent *et al.*, 2010; Wu *et al.*, 2010; Mihaljevič *et al.*, 2011 and Zuna *et al.*, 2011). These methods offer multi-element and isotope analysis with low detection limits, but relatively large amounts of wood sample are needed. In contrast, another group of methods are non-destructive, analyzing intact wood cores without digestion; for example, particle-induced X-ray emission (Legge *et al.*, 1984), synchrotron radiation X-ray fluorescence analysis (Goldberg *et al.*, 2007), energy dispersive X-ray fluorescence, (MacDonald *et al.*, 2011), and secondary ion mass spectrometry (Brabander *et al.*, 1999). This group also includes the laser ablation (LA) ICP-MS method (e.g. Hoffmann *et al.*, 1994; Garbe-Schönberg *et al.*, 1997; Watmough *et al.*, 1997; Witte *et al.*, 2004; Burnett *et al.*, 2007; Monticelli *et al.*, 2009 and Novak *et al.*, 2010). An important advantage of these microprobe-based methods for dendrochemistry is the relatively small amount of material required for analysis in comparison with wood digestion methods, which makes them ideal for analyzing tree rings and producing annually-to-seasonally resolved chemical records. On the other hand, because the sampled area of each tree ring is relatively small, issues related to the heterogeneity of tree rings can be amplified (compare Pearson *et al.*, 2005).

LA-ICP-MS has the added advantages of high spatial sampling resolution and low detection limits (Outridge *et al.*, 1995), which are beneficial, especially in the case of trees with very narrow growth rings. What is less clear, however, is how wood structure can impact the analysis and results. For instance, the variable structure of wood may affect how particular species react to the laser ablation process, and for some species with high intra-ring variation in element concentration, it may be quite inappropriate (Watmough *et al.*, 1997 and Watmough, 1999). The variable response of wood structure to the laser ablation process has to date been documented for only a small number of species, which limits the application and development of the technique for dendrochemical studies.

Preparation of tree-ring samples, the key to reducing contamination and maintaining consistent wood ablation, is a basic consideration of the laser ablation method. There is a need to find a compromise between preparing a tree core for visual counting of growth rings and laser ablation of the wood surface, while reducing contamination potential. Determining the optimum sample preparation technique for a given study species is a critical first step in the application of LA-ICP-MS to dendrochemistry.

Sample preparation for LA-ICP-MS is relatively straightforward and inexpensive (Watmough *et al.*, 1998b and Outridge *et al.*, 1995), but the investigation of a large number of old trees by the typical method of spot ablation can be highly demanding on machine time. In this context, the selection of the most effective sampling method — spot or line scan — that both meets the study goals and complements the type of wood structure is critical.

This study has two main objectives: 1) to determine a fast, reliable and cost efficient method of laser ablation of tree rings to reconstruct annually-resolved Pb concentrations from species that are found in St. John's; and 2) to analyze the effectiveness of the records generated from this laser ablation approach for interpretation of Pb levels.

2. BACKGROUND

Wood properties and structure are key considerations in choosing tree species for dendrochemistry studies. There are three main types of tree-ring tissue structures: coniferous (associated with coniferous tree species), ring-porous and diffuse-porous (both found in deciduous tree species). Coniferous tree rings mostly consist of tracheids that have large lumen diameters and thin cell walls in the earlywood and smaller lumina and thicker cell walls in the latewood (**Fig. 1a**). Coniferous tree species are generally considered more suitable for metal pollution studies because of this relatively uniform and simple wood structure that has relatively low permeability and low moisture content of the heartwood with associated low fluid flow (Cutter and Guyette, 1993).

Ring-porous wood is characterized by a highly differentiated tree-ring structure (**Fig. 1b**). The distinctive earlywood consists of one or more rows of large vessels that create a ring-like structure. The latewood is composed of smaller vessels, fibers, parenchyma, and in some species tracheids. Water transport in ring-porous species is limited usually to the outermost 1 or 2 annual rings and for this reason they are preferred by some for dendrochemistry (e.g., Baes and Ragsdale, 1981 and Hagemeyer, 1993).

Diffuse-porous wood has more uniform structure within its annual ring, with relatively small vessels more or less evenly distributed (**Figs. 1c**, **1d**). As a result, earlywood is not so easily distinguished from latewood. The uniform structure has been associated with low intra-ring variation in element concentration (e.g., American tulip tree (*Liriodendron tulipifera* L.) and maples (*Acer* sp.); McClenahen *et al.*, 1989 and Watmough *et al.*, 1997, 1998a, 1998b), which can be beneficial when microprobe analysis is used.

The microprobe technique in LA-ICP-MS means that the ablated area is small, sometimes even comparable with the elements of the wood structure. This fact, together with the variability observed in wood structure, dictates how a tree species will respond to the ablation process (Watmough *et al.*, 1997). Moreover, large structural differences can be observed even among species belonging to the same tree-ring structure type, which may significantly differentiate their response to the ablation technique. That is why every species should be carefully tested before it is used in dendrochemical studies involving LA analysis.

Although wood preparation is relatively simple and inexpensive for LA analysis, the potential for contamination is a serious concern, especially on the wood surface prepared for ablation. Usually tree core preparation involves sanding (e.g., Garbe-Schönberg *et al.*, 1997; Watmough *et al.*, 1997, 1998a, 1998b; Burnett *et al.*, 2007 and Novak *et al.*, 2010), but cut surfaces (Prohaska *et al.*, 1998) and unprocessed cores have been used (Witte *et al.*, 2004 and St. George *et al.*, 2006). During sanding, displaced wood particles may infill the lumina of vessels and tracheids on the core surface. The resulting contamination can affect not only the surface wood, but also the deeper parts of the prepared wood sample, depending on the size and length (depth) of the lumina (Pearson *et al.*, 2005). Some studies have taken the additional step to wash sanded cores in 10% trace HNO_3 followed by rinsing in double distilled water before analysis (Watmough *et al.*, 1997); there is, however, a chance for element leakage during this process.

Although preparation of the tree core sample by cutting produces clear cell structure, which is useful for tree-ring counting, surface contamination from the cutting tool can also be an issue. Consequently, an unprocessed tree

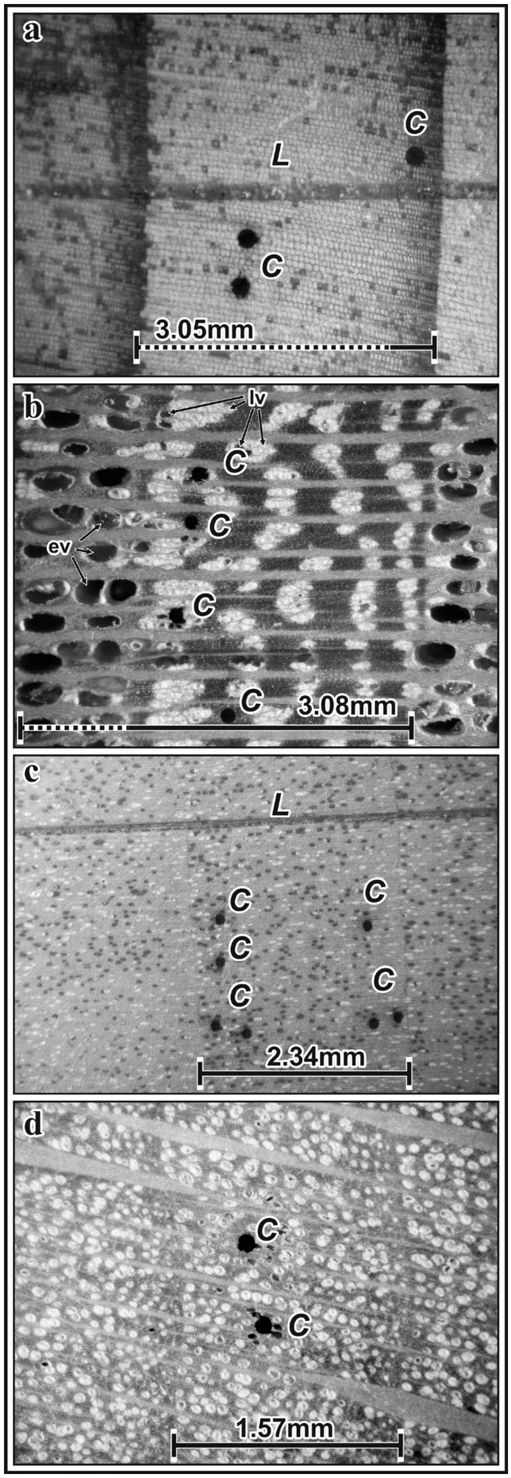

Fig. 1. *Photographs of wood structure from sanded tree cores sampled for this study: a) spruce (coniferous); b) elm (ring-porous); c) horse chestnut (diffuse-porous), d) beech (diffuse-porous). The width of a singletree ring is given for scale on each photograph, together with an approximate outline of earlywood (dotted line) and latewood (solid line) for spruce and elm. Spot ablation craters are identified with the letter C, whereas line scan ablation traces are marked with an L. For elm wood, earlywood and latewood vessels (pores) are denoted as ev and lv, respectively. Note irregularities in the shape of craters and the ablation of surrounding structures in elm and beech wood.*

core seems like the best compromise, but it too may harbour contamination from the borer used to extract the tree core. To minimalize the potential effects of contaminated wood surfaces during LA, commonly a surface wood layer is removed by ablation prior to the formal analysis (Hoffmann *et al.*, 1994; Garbe-Schönberg *et al.*, 1997; Prohaska *et al.*, 1998 and Monticelli *et al.*, 2009), an additional step that significantly increases the analytical time. Alternatively, other approaches simply discard the first part of the recorded signal (e.g., ~10 seconds, Burnett *et al.*, 2007), which is more time efficient and particularly appropriate when the ablation time is relatively long.

Spot ablation is the most common sampling method in LA analysis. One to several spots (craters) is normally ablated in each tree ring. Occasionally a grid of spots (Monticelli *et al.*, 2009) or a linear raster parallel to the growth rings has been used (St. George *et al.*, 2006 and Novak *et al.*, 2010). Although the LA method is fast and bypasses the tedious process of sample preparation necessary for other analytical approaches, the ablation of several spots within each ring of century-old trees can be time consuming (up to 6 weeks of laboratory time). Because it is critical in dendrochemistry to analyze more than one core from each tree and several trees from each site (to reduce local variability; Watmough, 1999), the duration and cost of analysis can be prohibitive for intensive studies. Another sampling option is available that involves continuous line scan ablation across the wood structure. To our knowledge this sampling approach has not been tested against the more traditional spot ablation in dendrochemical studies, although it is significantly more time efficient and can produce an order of magnitude more data points for the same effort.

In summary, our preparatory study for urban Pb dendrochemistry in St. John's addresses three research questions: 1) Does growth-ring structure affect the quality of the Pb signal in our available tree species? 2) Does line scan sampling of tree cores represent a more effective sampling procedure in LA-ICP-MS? and 3) Do tree-core preparation techniques significantly affect the quality of the Pb signal from LA-ICP-MS? These are basic questions that have not been addressed in the literature for the LA technique on the available tree species in St. John's. We are confident that the study results will benefit the analytical design of tree-sample selection and preparation for other dendrochemical studies using LA-ICP-MS.

3. STUDY AREA

St John's is an historic, light industrial, port city on the east coast of Canada (**Fig. 2**) with a relatively small population for a provincial capital (106,172; 2011 census). The city grew outwards from the harbour over the first half of the twentieth century (**Fig. 2**) and it is this older downtown core that has the greatest legacy of soil Pb contamination. While recent analysis has shown that more than half the residential soil sampled in the city (n = 1230) had Pb concentrations exceeding national health-based guidelines of 140 ppm, of greater concern were the exceptionally high concentrations (>1200 ppm) that tend to occur on residential properties that date to the 1920s or earlier (much of the downtown core; Bell *et al.*, 2010 and Foley *et al.*, 2011). These high soil lead levels cannot be attributed to any long-standing point source of Pb pollution but are the product of centuries of urbaniza-

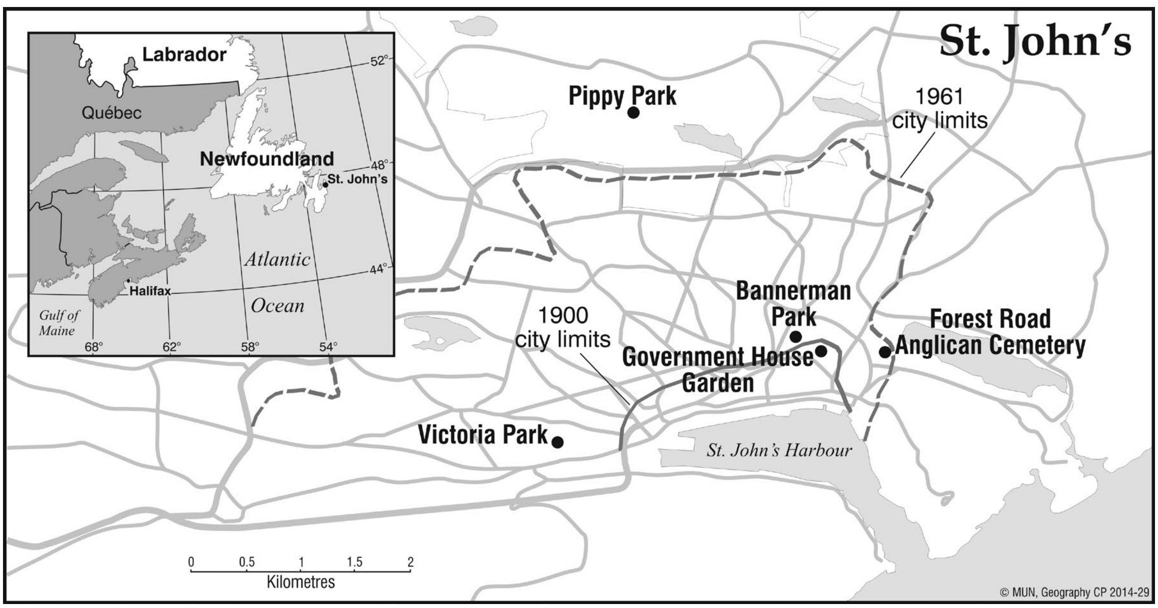

Fig. 2. *Location of dendrochemistry sample sites in St. John's relative to city limits in 1900 and 1961. The old downtown area surrounding St. John's harbour has a legacy of high soil Pb levels accumulated over a century of leaded exterior paint use, domestic coal burning and leaded gasoline use. Inset shows location of St. John's in Newfoundland and Labrador, eastern Canada.*

tion, together with traditional practices of painted clapboard housing and coal burning, both of which released Pb to the soil (Bell *et al.*, 2010).

An important goal of the *LeadNL* project is to assess the potential health effects of residential environmental lead exposure on the population of St. John's. To be able to reconstruct the historical lead burden over time, especially in the downtown core, would provide important temporal and spatial dimensions to the lead exposure risk assessment. Direct monitoring of lead particulates in air span only a short period between 1972 and 1998, while geochemical analysis and dating of urban lake sediments provide limited temporal and spatial resolution (Christopher *et al.*, 1993 and Christopher, 1999). In contrast, old trees growing in the downtown core and former outskirts of St. John's present a potential annually-resolved record of Pb levels in the city over past several centuries.

In the first stage of our research we were interested in finding the oldest trees that live in the oldest downtown area, where the highest lead levels in soil have been recorded (Bell *et al.*, 2010). All trees observed within this area represent non-native species; most of them were brought from Europe and have been planted since the mid-nineteenth century. The oldest clusters of trees are located in two public parks (Bannerman Park and Victoria Park) and also in the garden surrounding Government House (built 1831), the current residence of the Lieutenant Governor of Newfoundland and Labrador. The oldest are European beech (*Fagus sylvatica* L.) and horse chestnut (*Aesculus hippocastanum* L.) trees that are about 170 years old. Other relatively old trees are elm (*Ulmus* sp.) and sycamore maple (*Acer pseudoplatanus* L.; **Table 1**). Old coniferous trees in the downtown are rare; red pines (*Pinus resinosa* Ait.) about 100 years old for example are found in Forest Road Anglican Cemetery (**Fig. 2**). In contrast, abundant conifers grow in the boreal forest of Pippy Park, a fragment of natural forest protected for recreation within the city and located about 3 km from the downtown. The oldest trees (spruce and fir) there are more than 110 years old.

4. MATERIALS AND METHODS

In this section we present our rationale for the selection of study species and describe the sampling, preparation and analytical procedures used in the research design. Statistical measures and the format for results presentation are also outlined.

Species selection

In the process of species selection for this study, three requirements needed to be met: availability of old specimens in the downtown; demonstrated utility in dendrochemical studies; and suitability for the laser ablation technique. Taking into consideration the age of trees, the number available for sampling and their location within the city, the obvious first choice of study species were European beech and horse chestnut trees (**Table 1**). European beech is widely distributed in forests of Central Europe and is commonly used in dendrochemistry (e.g. Meish *et al.*, 1986; Hagemeyer and Schäfer, 1995; Watmough and Hutchinson, 2003; Bellis *et al.*, 2004 and Hojdová *et al.*, 2011). Horse chestnut, a native of the Balkan Peninsula, has been widely cultivated in parks and urban areas of Europe and has been commonly used for monitoring urban pollution (Yilmaz *et al.*, 2006) and the influence of roadside pollution on tree growth (Fostard and Pedersen, 1998). It has been rarely used, however, as a target species in dendrochemical studies of urban pollution (Ward *et al.*, 1974) and therefore inclusion in the St. John's study represented an additional test of its suitability.

The other relatively old tree species available in the St. John's downtown is sycamore maple (**Table 1**). Trees of the *Acer* genus are commonly used in dendrochemistry (e.g., Rolfe, 1974 and Cote and Camire, 1995), although with varying degrees of success (Watmough and Hutchinson, 1999, 2003 and Patrick and Farmer, 2006). Unfortunately, tree-ring sequences from two sampled maple trees only weakly correlated with each other and therefore cross-dating of rings was problematic, which made them unsuitable for further dendrochemical study.

Table 1. *The oldest tree species sampled in St. John's, by age. The trees were sampled in targeted areas of the city that escaped the last "Great Fire" of 1892 (Higgins, 2007). The tree-ring structure of each species is designated as follows: rp = ring-porous; dp = diffuse-propus; c = coniferous. NAR is the number of annual growth rings observed in cores. See Fig. 1 for location of sampling locations in St. John's.*

Species sampled	tree ring structure type	Location	NAR
beech (*Fagus sylvatica* L.)	dp	Government House Garden	158
horse chestnut (*Aesculus hippocastanum*L.)	dp	Government House Garden	154
elm (*Ulmus* sp.)	rp	Victoria Park	127
sycamore maple (*Acer pseudoplatanus* L.)	dp	Government House Garden	117
sycamore maple (*Acer pseudoplatanus* L.)	dp	Victoria Park	112
black spruce (*Picea mariana* (P. Mill.) B.S.P.)	c	Pippy Park	112
elm (*Ulmus* sp.)	rp	Bannerman Park	101
red pine (*Pinus resinosa* Ait.)	c	Forest Road Anglican Cemetery	96
balsam fir (*Abies balsamea*)	c	Pippy Park	96
sycamore maple (*Acer pseudoplatanus* L.)	dp	Bannerman Park	92

Elms found in two public parks in downtown St. John's represent ring-porous wood (**Table 1**). Species with this kind of structure are commonly used in dendrochemical studies because water transport usually involves the outermost annual rings only, which increases the temporal resolution of the dendrochemical record (Ault *et al.*, 1970; Cutter and Guyette, 1993; Eklund, 1995; Rao *et al.*, 2002; Prapaipong *et al.*, 2008 and Wu *et al.*, 2010). Perhaps related to this characteristic is the relatively high Pb accumulation noted in the ring-porous wood of oak and ash (Kardell and Larson, 1978). Does elm also display elevated Pb concentrations? Inclusion of elm in our study provided an opportunity to address this question.

In order to compare the results from the predominantly deciduous, older trees of downtown St. John's with the more commonly used coniferous species in metal pollution studies, we included black spruce (*Picea mariana* (P. Mill.) B.S.P.) trees from Pippy Park in our study (**Tables 1** and **2**). Unfortunately pine trees in downtown St. John's are rare and are much younger than the spruce in Pippy Park and so pine was not be used in the study.

Tree core collection and preparation

In this pilot stage of the dendrochemical project, tree cores initially collected in 2011/12 for aging of available trees species were re-used for testing wood and species reaction to the LA process (**Table 2**). The exception was a second tree core of horse chestnut (11gh_ah2, **Table 2**) that was collected in 2012 specifically to compare dendrochemical results from different wood preparation techniques. All tree cores were extracted from living trees using a Pressler borer at a height of approximately 1.3 m. Samples for age estimation were glued in wooden holders and cut using a preparation knife to reveal the tree-ring structure of the wood. The annual rings widths were measured using a Velmex measuring system with a precision of 0.005 mm.

In preparation for the laser ablation analysis, tree cores were cut into the 4-cm-long segments and mounted in either epoxy or clay to accommodate the instrument chamber cell. Cores mounted in epoxy were sanded to create a smooth surface for ablation. For comparison of core processing methods, a tree core was obtained using a Pressler borer rinsed with Analar acetone and then distilled water. First, unprocessed core pieces were ablated, then one side of the core was cut with a knife rinsed in acetone and the ablation repeated and finally, another side of the core was sanded and the surface ablated. The same tree core was used to avoid potential differences in element concentration around the tree bole (Patrick and Farmer, 2006 and Kirchner *et al.*, 2008). Horse chestnut wood was selected because preliminary results suggested a good response to laser ablation (see Results section).

Tree core ablation

We compared two methods of sample ablation. The popular spot ablation enabled deep wood penetration, although deeper spots required greater analytical time. Although there was no opportunity to monitor the depth of absolute ablation, the uniform length of the ablation period for each spot (50 seconds; **Table 3**) provided a degree of consistency in ablation exposure. The need to reduce costs led us to test another type of analysis, which continuously ablates along a line, perpendicular to tree ring boundaries. One of the advantages of the line scan method is the large number of data points that can potentially be recorded for one tree ring. Apart from the obvious benefits of a larger sample size on data accuracy and precision, it also helps address the issue of wood heterogeneity within tree rings. We used a 20 μm/s velocity for laser movement across the sample, which generated on average about 130 data points in each tree ring (**Table 3**). For comparison, the number of data points (spots) usually used in spot analysis is up to a dozen or so per ring. Again, we were not able to determine the depth of the line scan penetration in the wood but as the ablation exposure time was less (calculated from average parameters in **Table 3**), the depth of penetration relative to spot ablation was also presumably less. To test the two ablation techniques and specifically to gauge the effects of laser beam penetration on different wood structures, spot and line scan ablation were performed on cores from three species: black spruce, elm and horse chestnut (**Tables 2** and **3**). The laser beam diameter was roughly similar for the spot (99 μm) and line scan (89 μm) analyses, with differences based on operator experience with and preferences for the instrumentation (**Table 3**).

Table 2. *Study design matrix indicating the study species and tree samples used in the comparative analysis of sample preparation procedures, ablation methods, and ablation responses to wood structure type. Note: horse ch. = horse chestnut, irv = intra-ring variability.*

species	Sample code	Sample mount		Sample preparation			Ablation method		Ablation response	
		epoxy	clay	unprocessed	cut	sanded	spot	line	visual	irv
beech	11gh_fs1	x				x	x		x	
spruce	11pp_p1	x				x	x	x	x	x
elm	11vp_u1	x				x	x	x	x	x
horse ch.	11gh_ah1	x				x	x	x	x	x
horse ch.	11gh_ah2		x	x	x	x		x	x	x

Table 3. *Laser parameters employed for spot and line scan ablation of wood for this study.*

Laser parameters	Spot	Line scan
Laser beam diameter (µm)	99	89
Laser beams for reference materials (µm)	49	49
Laser beams for cellulose standard (µm)	40	40
Ablation time (s)	50	420–780
Average line length (mm)	---	10
Gas blank (s)	20–30	20–30
Energy density (J/cm^2)	4	4
Repetition rate (Hz)	8	8

Instrumentation, standards and results presentation

Analyses were carried out using a Thermo Element XR, high resolution, double focusing, magnetic sector ICP-MS attached to a GeoLas 193 nm Excimer laser system. Helium carrier gas transported the ablated material to the ICP-MS at a flow rate of about 1 to 1.2 L/min. Argon sample gas was mixed with the sample stream just before it entered the torch. Time-resolved intensity data were acquired by peak-hopping in a combination of pulse-counting and analogue modes, depending on signal strength, with one point measured per peak. Carbon was used for internal standardization. The carbon content for the in-house cellulose standard (see below) was 44.4% and for the tree species analyzed was estimated using Lamlom and Savidge (2003). The analytical sequence typically used 5 reference/calibration standards at the start, followed by 3 samples or unknowns, 2 standards, 3 samples or unknowns, and so on, finishing with 4 standards at the end.

Reduction, processing and graphing of laser data used the Iolite software package (Woodhead *et al.*, 2007 and Paton *et al.*, 2011), which runs on the Igor Pro platform (Wavemetrics, Inc., Oregon, USA). Processing through Iolite included background subtraction, selection of representative signal intervals for integration, internal standard correction for ablation yield differences, correction for instrument sensitivity drift during the analytical session, and conversion of count rates (counts per second) to concentrations by reference to the calibration standard. Each analysis consisted of about 20 to 30 seconds of background data (gas blank; used for background correction) and the ablation signal once the laser had fired.

The standard was prepared by spiking α-cellulose powder (Sigma-Aldrich Canada Ltd, Oakville, Canada) with a multi-element solution. While Pb was the element of primary interest in this study, the cellulose was spiked with multiple elements to support related studies. Approximately 2 g of cellulose was placed in 15 ml of a 50-ppm multi-element solution containing a mixture of 29 elements in 0.3N HNO_3 (SCP28AES and U ICP standard, SCP Science, Baie-D'Urfé, Canada). The mixture was magnetically stirred for three hours. The wet cellulose mixture was then centrifuged and the solution was decanted. After air-drying, the resulting cake was ground into a fine powder with an agate mortar and pestle. The spiked powder was then pressed into a pellet with an XRF pellet press. To determine the elemental concentration of the spiked pellet, three fragments of the pellet (approximately 100 mg each) were placed with several millilitres of 8N HNO_3 in individual sealed PFA beakers on a hotplate until the cellulose was fully digested. The solutions were then diluted with double deionized water and analyzed by ICP-MS. The average concentration of Pb in the three pellet fragments was 131 ppm ± 6 ppm (1 SD).

The range of Pb values from multiple spot ablations (2–4 spot ablations in earlywood and latewood) of randomly chosen tree rings were used to evaluate intra-ring variability in the study species. To standardize results between tree rings, the range of values for each tree ring was divided by the mean of all values recorded for a single species. Results are expressed as a dimensionless ratio. Variability in Pb concentration from line scan ablation measurements within an annual tree ring is presented as the coefficient of variation (CV) of measurements from a single ring, which is the standard deviation expressed as a percentage of the average value for each ring. Tree-ring data were properly aligned using standard dendrochronological procedures (Cook and Kariukstis, 1990) but are unconventionally presented here as consecutively numbered rings starting at the pith. This format is chosen for ease of presentation because an absolute chronology (calendar years) is not required at this stage of the study.

5. RESULTS AND DISCUSSION

Reaction of selected species to laser ablation

Visual analysis

Visual observations revealed differences in the reaction of wood of different species to laser ablation. Upon spot ablation, spruce and horse chestnut wood produced regular shaped craters (**Figs. 1a**, **1c**), whereas those in elm and European beech were irregular, resulting in ablation of surrounding wood beyond the targeted zone (**Figs. 1b**, **1d**). These irregular ablation craters can result in higher or lower element concentrations than expected depending on whether the additional ablated wood is more or less concentrated in the element. The shape of craters in the vertical plane can also be irregular given the three-dimensional heterogeneity of wood structure.

Anatomical wood structure can explain the differences in the reaction of specific species to ablation. Spruce and horse chestnut have relatively uniform structure. Although the tracheids of the coniferous spruce vary in lumen size and cell wall thickness across each ring (see Background section), there is a consistent pattern within earlywood and latewood components and therefore wood ablation is regular. In horse chestnut, a diffuse-porous species, the relatively small vessels are evenly distributed within rings and consequently produce a circular ablation crater. In contrast, the other diffuse-porous species — European beech — has a distinctly higher number of bigger vessels within a ring and as a result the laser beam tended to ablate material from more than one vessel at a time, producing an irregular ablation crater. For this reason, we abandoned the use of European beech at an early stage of the study based solely on the results of the spot ablation. The ring-porous wood of elm has a highly differentiated ring structure. Earlywood consists of big vessels, one or more of which may be ablated by the laser beam producing an irregular crater. The occurrence of smaller vessels in the latewood of elm is patchy and the shape of the ablation crater is therefore dependent on whether the targeted area intersects one of these patches. If it does, then craters tend to be more irregular.

Intra-ring variability of Pb concentration

Our sampling design permitted an examination of intra-ring variability in the three study species using both targeted spot ablation, with up to four spots per ring distributed across a range of wood structures in individual rings, and line scan ablation that generated on average 130 individual readings across the full ring width (**Table 2**). Using the range of values recorded for a single ring as a measure of the variability within the ring, expressed as a dimensionless ratio, our results show that spruce and horse chestnut had comparable and relatively low variability, with an average range of 0.30 and 0.28, respectively, from 12 randomly selected rings. For elm rings, these values were markedly higher, with an average of 0.73 (**Fig. 3**). The results of the line scan analysis confirmed the findings from the spot analysis in horse chestnut, but were at odds with those in spruce (**Fig. 4**). In fact, the mean CV values for both spruce and elm were similar and roughly twice as high as horse chestnut (38.7%, 39.9% and 19.7% respectively).

The low intra-ring variability in Pb levels for horse chestnut is consistent with previous findings for diffuse-porous tree species with similar wood anatomy such as maples (Watmough *et al.*, 1997, 1998a, 1998b) and American tulip tree (McClenahen *et al.*, 1989). Meanwhile, the high intra-ring variability in Pb levels for elm is somewhat typical for this type of ring-porous wood structure; for example, bur oak (St. George *et al.*, 2006) and red oak (Brabander *et al.*, 1999). In both species of oak, the relationship between wood structure and intra-ring variability is well illustrated.

Spruce produced inconsistent results for intra-ring variability between ablation methods. The relatively uniform wood structure in spruce should produce low intra-ring variability in Pb levels, as observed here in the spot ablation results. In contrast, the line ablation method produced higher intra-ring variability in Pb levels that may be explained by the wood density contrast between earlywood and latewood in spruce, producing an irregular ablation surface (cf. Nowak *et al.*, 2010 — reported difficulties with obtaining the properly even surface of the early wood) and potential plucking of large wood particles during the ablation process (cf. Monticelli *et al.*, 2009). Of note, other studies of element distribution in coniferous species have shown significant differences in concentrations between earlywood and latewood (e.g., pine — Hoffmann *et al.*, 1994; cedar — Monticelli *et al.*, 2009).

Wood sample preparation

Comparison of lead levels (CV) between three preparations (unprocessed, cut, sanded) of the same horse chestnut tree core did not show any clear differences (**Fig. 5**). The averaged CV values for each preparation over the 100-year record were similar (17.5%, 20.5% and 20.4% for unprocessed, cut and sanded preparations, respectively). This suggests that the precision (data point distribution for a single measurement) of the ablation procedure is not related to the preparation process. Similar patterns in lead concentration, with four distinct peaks, are apparent in the records from all three preparation procedures (peaks B, C, D, and E, respectively in **Fig. 6**). There is little consistency, however, in the relative magnitude of Pb levels by preparation in each of the peaks. Only in peak E do all three techniques record the same level of Pb concentration (4–5 ppm). In two of the

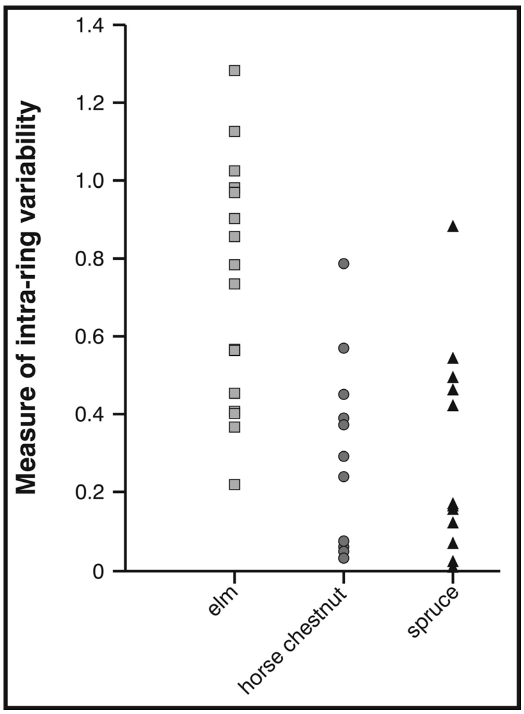

Fig. 3. *Comparison of intra-ring variability in 12 randomly selected tree rings in elm, horse chestnut and spruce tree core samples using the range of Pb values recorded from 2–4 spot ablations in earlywood and latewood (see text for derivation of intra-ring variability ratio). In general, elm (mean value: 0.78) tends to exhibit higher ratios than spruce or horse chestnut (mean value: 0.30 and 0.28, respectively).*

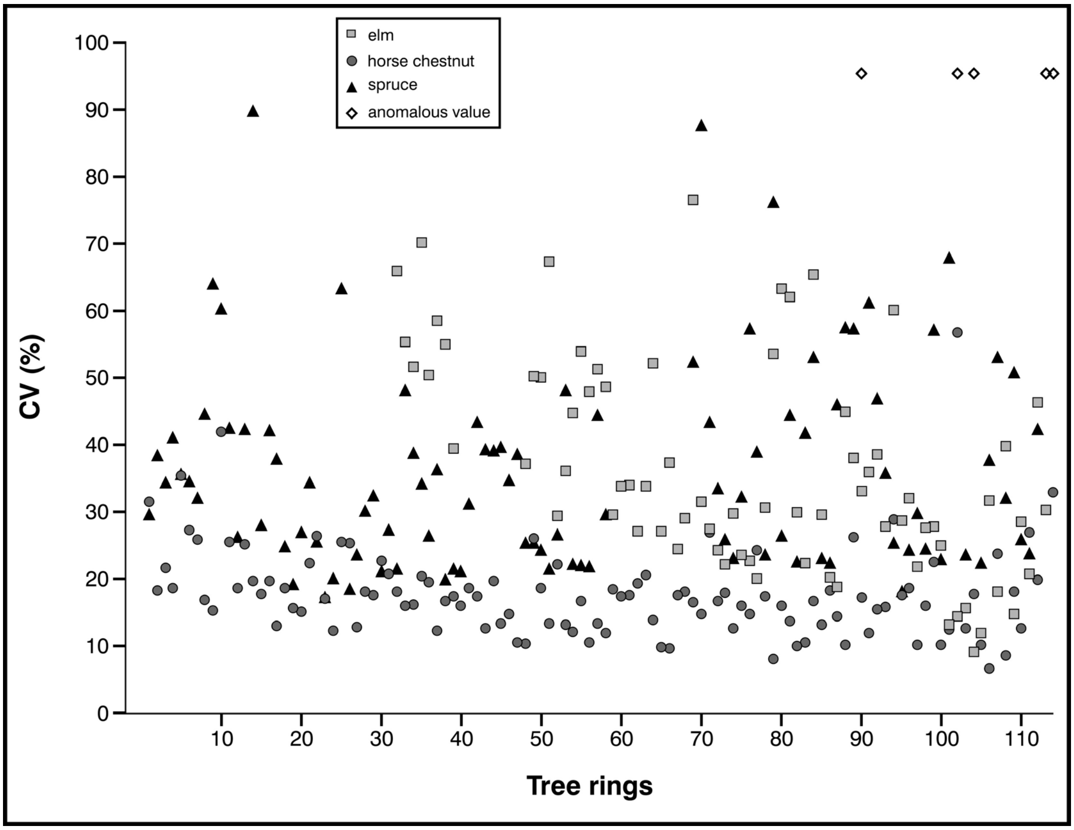

Fig. 4. *Comparison of coefficient of variation (CV) values from line scan ablation of temporally overlapping tree-ring records from elm, horse chestnut and spruce tree cores (modified from Danek et al., 2014). CV is the standard deviation expressed as a percentage of the mean value. Each tree-ring value is based on about 130 data points. Anomalously high values (100–300%) occur in all species and are represented by a diamond symbol. Horse chestnut had on average the lowest CV value (19.2), almost half that of spruce and elm (38.7 and 39.9), respectively.*

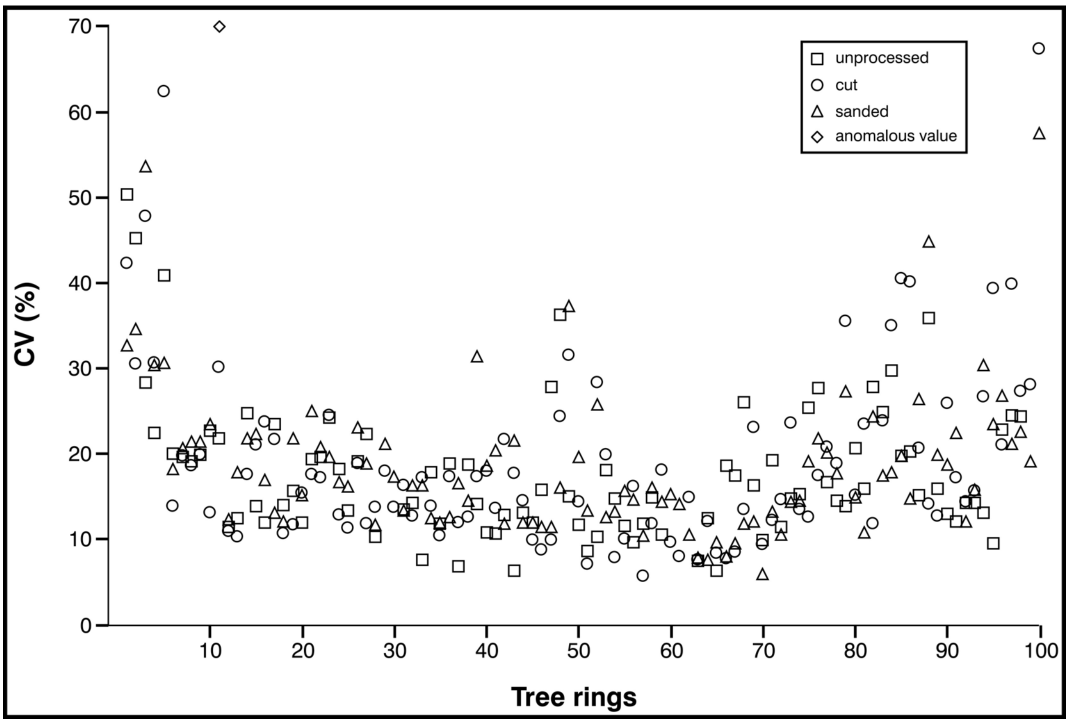

Fig. 5. *Comparison of coefficient of variation (CV) values for the same horse chestnut tree core (11gh_ah2) line scan ablated on unprocessed, cut and sanded surfaces. The diamond symbol denotes one anomalously high value (100%) for the sanded preparation. There are no distinct differences in the data for the three sample preparations and mean value for the 100-year record for each preparation type is similar (17.8%, 19.2% and 19.6%) for unprocessed, cut and sanded preparations, respectively.*

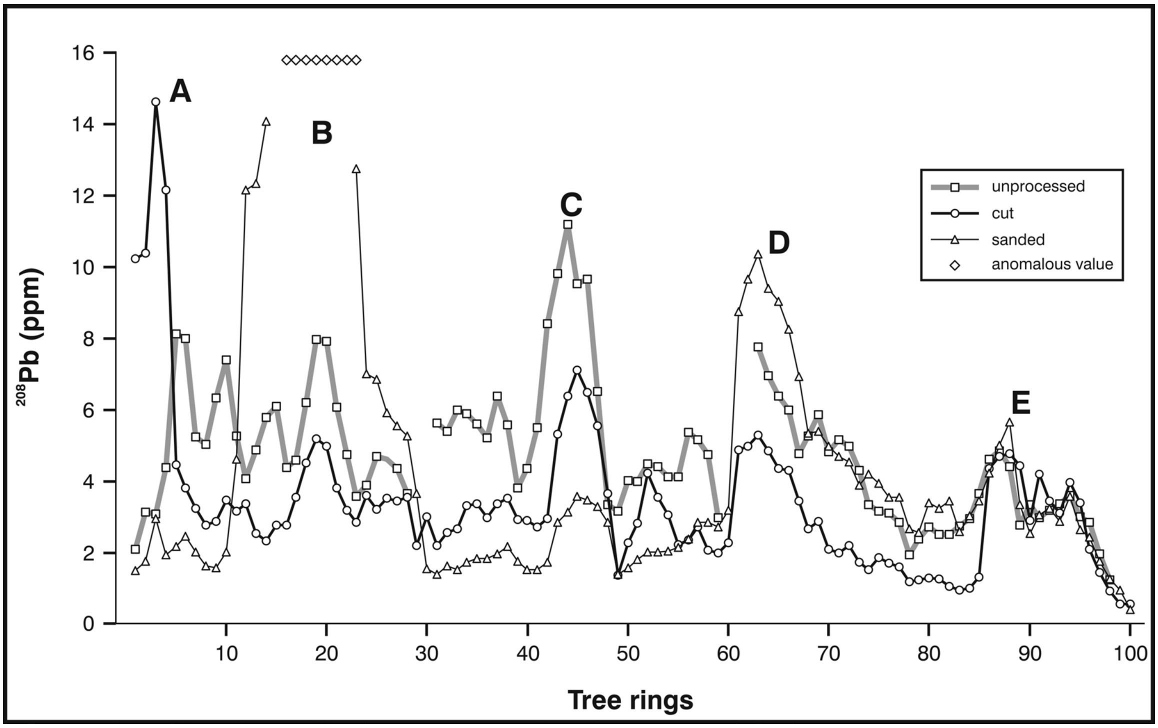

Fig. 6. *Comparison of Pb concentrations (ppm) for the same horse chestnut tree core (11gh_ah2) line scan ablated on unprocessed, cut and sanded surfaces. Note that the record is a composite of the analyses of 4-cm-long segments of the horse chestnut tree core. Diamond symbols denote anomalously high concentrations between 19.7 and 44.3 ppm for the sanded preparation. Five concentration peaks A–E are discussed in the text.*

other peaks, the sanded sample concentration exceeds those of the unprocessed and cut samples by 33% and 100% (peak D) and 450% and 780% (peak B), respectively. Clearly the Pb concentration in peak B for the sanded core is anomalous for the entire record — no matter which preparation technique is examined — and will be further discussed below. The unprocessed core produces the highest Pb values in peak C, exceeding the cut and sanded samples by 60% and 260%, respectively, and records the highest background (between peaks) levels in the 60 oldest tree rings. The unprocessed core record also displays the greatest inter-annual to inter-decadal variability in Pb concentration, particularly during this earliest tree-ring period. Only in peak A does the cut core produce the highest Pb levels (14 ppm), almost synchronous with the Pb record from the other preparation techniques.

Elevated and inconsistent levels of Pb in the unprocessed core sample may be attributable to two error sources. First, cores collected from trees have a round cross-sectional shape and because of the drilling process their surface is uneven and ragged. During laser ablation, larger wood particles can sometimes be pulled off from the core surface and lead to unreliable results (Monticelli *et al.*, 2009). This risk is higher for unprocessed cores. Second, the uneven surface of the unprocessed core may cause the laser to penetrate the sample to varying depths, which may lead to disparities in the amount of ablated material. This in turn may produce higher and temporally variable background Pb levels. The possibility of surface contamination from the borer itself during core extraction from the tree seems doubtful in the case of Pb because borers are mainly made of stainless steel with some hardeners such as tungsten (Shepard and Witten, 2005).

Maximum values and shapes of the peaks of elevated Pb concentrations observed in area D and particularly in area B of the sanded core sample may be related to spreading of wood dust during the sanding process, as was observed in other studies (Monticelli *et al.*, 2009). Fine particles of wood dust can fill large vessels and other wood elements and are subsequently ablated during analysis, which depending on the Pb concentration of the dust, may amplify or reduce the expected results for that area of the ring. During background (between peaks) periods when overall wood Pb levels are low, the sanded sample produces the lowest Pb concentrations, which may lend support to the "wood dust" effect. Similarly, the anomalously high Pb level in peak B for the sanded sample may be attributable to an extreme "wood dust" effect associated with a period of elevated Pb levels (5–8 ppm) during this period. In general, our results for the sanded core caution against the use of sanding as a preparation technique for laser ablation to avoid the contamination effects of wood dust. Even though this result was anticipated from previous observations (Monticelli *et al.*, 2009), our comparative test illustrates the magnitude of the contamination issue from wood dust, especially relevant given that sanding is commonly used in many laser ablation dendrochemistry studies.

The cut core sample produces the least elevated Pb levels in peaks B and D and is generally the middle value of the three for background Pb concentrations. The cutting technique prevents production of wood dust, limits crushing of cell structure during laser rastering (Pearson *et al.*, 2005) and reduces any contamination effect from the tree borer. At the same time it generates a flat surface that limits signal disturbances associated with irregular ablation penetration of ragged surfaces. On the other hand, the cutting procedure can be a source of contamination from the knife. In our analysis, although the risk of Pb contamination from knife seems to be very low (Shepard and Witten, 2005), it may be a possible explanation for peak A, which is not mirrored in the unprocessed and sanded wood records. To limit the possibility of contamination, rinsing the cutting blade in acetone, as we did, is recommended. Another explanation for peak A could be a discoloration observed in this part of the tree core, probably the effect of injury or infection that changed the wood properties. Such disturbances can radically increase element concentrations in tree rings (Watmough *et al.*, 1998b; Smith and Shortle, 1996). It does not, however, explain why a similar peak is not observed in the other two core preparations.

In conclusion, the preferred tree core preparation technique for laser ablation analysis of Pb concentration is cutting, which avoids the generation of wood dust from sanding and the ablation complications and contamination threat associated with an unprocessed core. Analysis of both sanded and unprocessed cores tends to produce extreme high and low background and elevated peak Pb values. In contrast, cut cores produce less variable records on short (inter-annual) and long (decadal to century) time scales. Caution should be exercised, however, to reduce potential contamination effects from the cutting instrument. The contamination issues associated with sample collection and preparation for LA-ICP-MS analysis can be eliminated altogether through pre-ablation of the wood surface; unfortunately, this solution would result in substantially increased laboratory costs and may not be practical for most dendrochemical studies.

Laser ablation process

Our comparative analysis of spot and line scan ablation techniques was designed primarily to select an available tree species that would demonstrate a consistent and reliable wood reaction to the ablation process. The strong dependency between a simple, uniform tree-ring structure and consistent Pb concentrations means that care must be taken in selecting an ablation process that matches the study species and goals. Species with complex wood anatomy or marked differences between earlywood and latewood structure require careful sampling attention, particularly if using the spot ablation technique. For example, our results (**Fig. 3**) support the observation of elevated element concentrations in the earlywood of ring-porous species (cf. St. George *et al.*, 2006), the magnitude of which may be dependent on element and overall pollution trend (Brabander *et al.*, 1999; Monticelli *et al.*, 2009). In general, spot analysis permits detailed and targeted studies of tree-ring structures. For example, if it were anticipated that the main source of pollution information is contained within intra-ring compositional differences, spot analysis would seem to be the most reasonable approach (Monticelli *et al.*, 2009).

In contrast, the application of line scan ablation provides the opportunity to generate an average element concentration for a full tree ring by fast and dense (100 data points per mm) multi-element measurement. For reconstructing annually resolved element concentration history from trees, for example, the line scan method is ideal and to some degree mitigates the complicating issue of intra-ring variability by averaging the signal across hundreds of data points and permitting more robust data processing to eliminate the most unstable, noisy parts of the signal.

A practical issue in the application of the line scan method is the correct age assignment of ablation results. As tree rings are identified and ring widths measured only after the line scan ablation is performed, there is potential imprecision in assigning data points to tree rings. Another issue is the accurate synchronization of the laser operation and the manual designation of start (following warm-up period) and end records (following laser stop) of the line scan. This technical procedure should be better harmonized in the LA system, but in practice the issue is less significant for analyses focused on multi-decadal to centennial records.

Other study considerations

The results or our experimental design study indicate that the best data for reconstruction of Pb concentrations through time in St. John's will come from line scan analysis of cut cores from horse chestnut trees. Comparison of Pb concentrations from two horse chestnut trees using the same wood preparation (sanded, which is not our preferred preparation) and ablation analysis (line scan) argues against overreliance on a single tree to provide a representative record for community-wide Pb levels (**Fig. 7**; compare Smith and Shortle, 1996 and Watmough, 1999). There is almost no correspondence between the two Pb records, with large departures in Pb levels and trends. For example, peak C in tree #2 coincides with a trough in the Pb record of tree #1, representing up to 40 times difference in Pb values. Also, peak D in tree #2 coincides with a period of relatively unstable but consistently lower Pb levels in tree #1. Over the last 30 tree rings the two Pb records mirror each other in displaying a general decline in levels but the record in tree #2 is less stable and 2–3 times higher in concentration. Although not specifically the focus of this study, there is the possi-

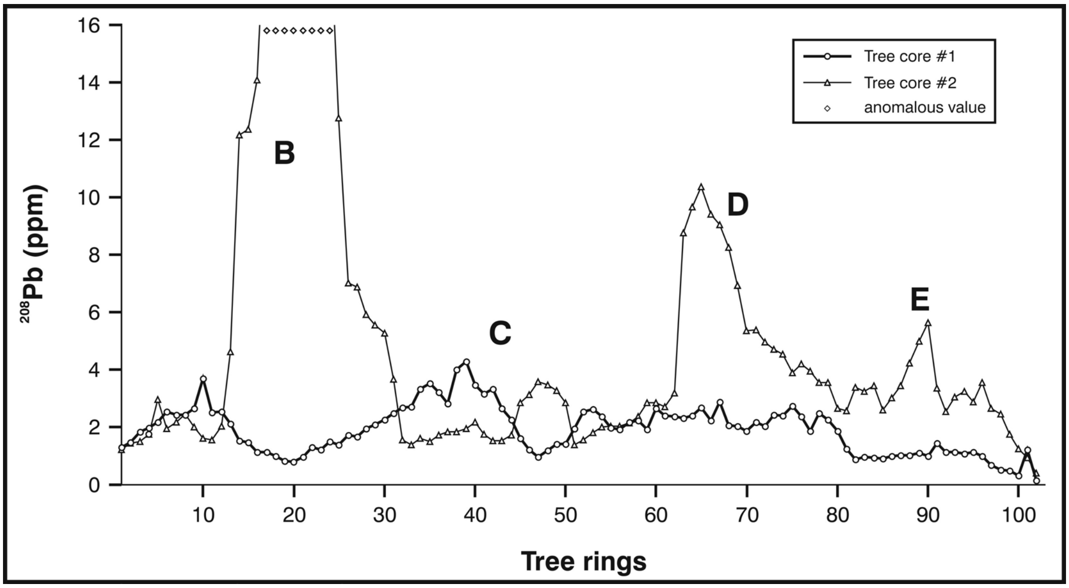

Fig. 7. *Comparison of Pb concentrations (ppm) from line scan ablation of two wood cores from nearby horse chestnut trees. Tree core #1 is sample 11gh_ae1 that was divided into 4-cm-long segments and mounted in epoxy and sanded. Tree core #2 is sample 11gh_ae2 that was also divided into 4-cm-long segments and then sanded and mounted on clay. Diamond symbols denote anomalously high concentrations between 19.7 and 44.3 ppm.*

bility that these dissimilar Pb records from nearby horse chestnut trees are partially a product of the medium on which the two cores were mounted. Cores from tree #1 were mounted in epoxy in preparation for laser ablation, whereas those from tree #2 were mounted in clay. According to Burnett *et al.* (2007), epoxy tends to infiltrate wood pore spaces and contribute a significant Pb blank. In their study, Burnett *et al.* examined ring-porous oak and hence this effect may be particularly strong in this wood structure where large vessels dominate earlywood. In contrast, horse chestnut has much smaller vessels and the effect may be less important. In addition, the Pb records displayed in **Fig. 7** are from sanded cores and it is expected that surface sanding and polishing would remove outer layers of wood and epoxy-filled vessels. On visual examination of our sanded horse chestnut cores, however, epoxy-filled and dust-filled (dust would be a mixture of wood and epoxy) vessels are still present at the surface, likely because of their cell structure depth. Consequently, laser ablation of the surface of epoxy-mounted cores are likely to record significant Pb blanks that may in part explain the differences in the two Pb records in **Fig. 7**. As a result of this observation, cores will only be mounted in clay for the full-scale St. John's study.

Previous dendrochemical studies have demonstrated that variation in element concentration between tree rings of the same calendar year from trees of the same species growing close together are common (e.g. Eklund, 1995; Garbe-Schönberg *et al.*, 1997 and Kirchner *et al.*, 2008). Consequently, published records of element concentration from dendrochemical studies are typically based on the analysis of two or more cores per tree and more than one tree of the given species per site, which generates more statistically robust trends (Smith and Shortle, 1996 and Watmough, 1999). The marked difference in Pb concentrations derived from only two cores from two different horse chestnut trees in this study reinforces this cautionary approach in dendrochemistry and argues strongly for more rigorous sampling replication and analysis using the procedures recommended from this current study.

6. CONCLUSIONS

In this preparatory study for the application of LA-ICP-MS for urban Pb dendrochemistry in St. John's, horse chestnut was determined to be the best of the available tree species because it exhibited a good response to laser ablation and produced the lowest intra-ring variations in Pb concentration. Preparation of the tree core using a knife produced the most consistent Pb concentrations. Although our comparison of three preparation procedures showed that all approaches have their disadvantages, the cutting method is significantly better than either sanding or leaving unprocessed. Tree cores selected for laser ablation should be mounted in clay to avoid infiltration of wood structures by a mounting medium that potentially introduces Pb blanks. Line scan ablation of tree cores is a relatively fast and inexpensive method for the study of Pb concentration over time. In contrast to spot ablation, it can generate hundreds of measurements per tree ring, which makes robust data processing possible and in turn reduces the influence of intra-ring noise. Procedural issues persist, however, and further refinement is necessary before widespread adoption. Consistent with recommendations from other investigations, our analysis strongly argues for the use of multiple cores from multiple trees of a single species for robust dendrochemical studies.

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