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ORIGINAL ARTICLE

Elemental line scanning of an increment core using EDXRF: From fundamental research to environmental forensics applications

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Abstract

Environmental forensics seeks to determine the responsible parties for contamination from leaks or spills of petroleum or other toxic products. Dendrochemistry contributes to environmental forensics at the intersection of analytical chemistry, tree biology, and environmental responsibility. To be useful, dendrochemistry requires the rigorous application of analytical techniques as well as an understanding of tree biology. The choice of analytical technique is usually driven by tradeoffs among the selection of chemical elements or molecules of interest, sensitivity and discrimination, spatial resolution, ease of sample preparation, availability, sample destructiveness, and cost.

One useful solid-state spectroscopic technique for dendrochemical analysis is energy dispersive X-ray fluorescence (EDXRF). This method provides essentially non-destructive, simultaneous detection of a number of elements with an adjustable spatial resolution, typically from 0.1 to 0.3 mm. The most commonly targeted elements are S and Cl as markers for fossil fuels, Cl for solvents, and Pb for leaded gasoline. Other metal elements may also be used as indicators of mining and smelting.

For elements that are not normally present in appreciable amounts in wood, the mere presence of the element anywhere in the tree-ring record indicates exposure of the tree to an unusual chemical event or process. Dating the environmental exposure from dendrochemical analysis can be complicated by internal changes in tree chemistry due to wood infection, tree maturation, and wood maturation.

Keywords: Environmental monitoring; Dendrochronology; Dendroecology; Dendrochemistry; Soil and ground water contamination

Introduction

Soil and ground water have become contaminated through the widespread use of petroleum for automobiles and industry. The costs surrounding the investigation and cleanup of such problems are often daunting and are increasingly being shared among responsible parties. In today's litigious world, numerous methods are used to identify parties responsible for soil and ground water contamination. Environmental forensics applies technical expertise to resolve disputes concerning responsibility for the costs of environmental cleanup.

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This expertise can be found in many fields, ranging from dendrology and geology to aerial photography and petroleum fingerprinting.

Dendrochemistry, the chemical analysis of precisely dated tree rings, can estimate the timing of the release of environmental contaminants such as gasoline or other petroleum products from an underground tank or pipeline (Balouet and Oudijk, 2006; Balouet et al., 2007). The conceptual model is that upon the release of a chemical into the environment, particularly a chemical that is normally absent or present in only small quantities in the soil, the chemical is taken up by the tree roots and enters the translocation stream conducted through the wood. Some amount of the chemical is either incorporated into the wood structure or bound to the surface of wood cell walls. This incorporation or fixation ideally occurs in wood formed during the same year as the environmental release. Alternatively, the chemical may be bound to wood already formed that is also conducting sap. The time of formation of wood that contains the chemical can then be used to infer the timing of chemical changes in the soil that can then be further related to the timing of the environmental release. Estimates of the release date can then be used to help determine responsible parties.

In this article, we provide information on energy dispersive X-ray fluorescence (EDXRF) analysis and limitations for use in forensic investigations of this type, including one case study.

Dendrochemistry

Traditional wood chemistry investigates physical properties, organic extractives, pulping characteristics, and performance of wood in service. These investigations generally are conducted on wood extracts or digests (Brown, 1967; Rowell, 1984). Dendrochemistry differs from traditional wood chemistry in that the research samples are obtained from precisely dated tree rings and that the research questions usually concern the timing of chemical changes in the external environment of the tree (McLaughlin et al., 2002; Watmough, 2002). When those environmental changes become the basis for a legal dispute, dendrochemistry can become a forensic tool to resolve the questions of exposure and timing (Balouet, 2005).

For applications in environmental forensics, dendrochemical analysis would ideally require minimal sample preparation and be non-destructive, be accurate and precise for both the chemical analysis and the dating of calendar year of wood formation, sufficiently sensitive to detect low quantities of the target compounds, be conducted at ambient air pressure to avoid volatilization of other compounds of interest, and able to discriminate between the target and non-target compounds. Additional concerns include availability of the equipment, time required for sample preparation and analysis, ease of data capture following analytical measurement, cost, and size limitations for the sample.

Many environmental releases that affect soil and ground water consist of organic chemicals, such as gasoline, diesel fuel or chlorinated solvents. Chlorinated solvents are taken up by the root system of trees (Schumacher et al., 2004) as are lead (Pb) and manganese (Mn) that were historically added to gasoline to improve engine performance (Gibbs, 1990; Stout et al., 2006). Other elements that occur naturally or are added to gasoline include boron (B), nickel (Ni), and phosphorous (P) (Gibbs, 1990; Kaplan et al., 1997). Sulfur (S), mostly in the form of natural hydrocarbons such as dibenzothiophenes, was also a significant component of diesel fuels and heating oils, comprising up to 2% of these petroleum products. These elemental markers can be identified in wood tissue and can contribute to the estimation of the time of tree exposure to the contaminant.

Over the past 2 years, we (J.C.B. and G.O.) have used these dendroecological methods to decipher contaminant releases and estimate their time frames at 23 sites in the US (California, New Jersey, Massachussets, and Pennsylvania) and France. These sites included releases of heating oil, gasoline, and chlorinated solvents. For the two sites at which historical corroboration was available, dendroecological evidence matched to the year the dates at which the releases were independently known to have occurred. Our dendrochemical interpretations have also been supported by calculations of ground water travel-time and the identification of time-specific gasoline additives. Some of these data are presently being used in litigation proceedings.

Analytical method

EDXRF has been used for dendrochemical analysis (e.g., Selin et al., 1993, Lindeberg, 2004; Devall et al., 2006). As with any spectroscopic method, EDXRF relies on fundamental characteristics of elements in the periodic table. The atoms of each element have a specific number of protons (the atomic number) balanced with an equal number of electrons. Conceptually, the electrons of each atom are arranged in concentric orbital shells that surround the atomic nucleus. The shells closer to the atomic nucleus contain electrons at a lower energy level than electrons in outer orbital shells. In EDXRF, the forensic sample is exposed to X-rays that excite the constituent atoms sufficiently to eject electrons from inner orbital shells. The ejected electrons are replaced by electrons from outer orbital shells. The energy lost by the electron in the transition from an outer to the inner shell is emitted as a photon.

The wavelength of the emitted fluorescent light is characteristic of the element. The number of emitted photons or "counts" corresponds to light intensity and is proportional to the element concentration. Unless specially calibrated, the counts indicate relative rather than absolute concentrations.

The wood matrix can affect the EDXRF results, particularly from matrical heterogeneity due to ring boundaries or variability within individual rings such as the structural differences between earlywood and latewood. As the wood matrix has a low mean atomic number (Z), counts can be adjusted for matrix effects through Compton correction, based on the scattering of X-rays due to the inelastic, incoherent interaction with the outer electrons of the matrix atoms (Garivait et al., 1997; Stephens and Calder, 2004). EDXRF can measure element composition at set distances (usually at a beam size of 0.1 mm and a spacing interval of 0.1–0.3 mm) along a vector on the surface of a dendrochemistry sample.

EDXRF analyzes solid materials such as increment cores and does not require sample digestion or solvent extraction. Analysis is conducted at ambient pressure and can accommodate intact cores. The core surface requires no special processing other than that required for standard dendrochronological analysis. The tree rings are exposed to controlled, low levels of energy, resulting in little or no sample destruction during analysis. Low irradiation energy also tends to improve repeatability (precision) and to minimize broadening of the elemental peaks.

The detection limits (DL) for EDXRF are related to Z, beam size, and duration of the counting time. For elements with $Z > 23$, measured with a beam size of 0.1 mm and a counting period of 10 s, $\mathrm{DL} \leqslant 10$ ppm. For elements with $Z = 13$–23, DL can range widely, decreasing with increasing Z (e.g., Si at approximately 700, S about 80, Cl about 50, and K about 15 ppm). The DL can be reduced by increasing the duration of X-ray exposure or by increasing the beam size. The decrease in DL is a function of the reciprocal of the square root of the increase in counting time (e.g. a 9-fold increase in counting time reduces the DL by a factor of 3). EDXRF is not usually applicable for very light elements with $Z < 13$.

We used an ITRAX X-ray fluorescence scanner (Croudace et al., 2006) to obtain EDXRF data for elements associated with petroleum fuel contamination from a single core of tulip-poplar (*Liriodendron tulipifera*). This core was collected as part of a successful forensic investigation to estimate the date of a combined gasoline and diesel fuel release in New Jersey (Balouet and Oudijk, 2006). This present report adds elements that may be of interest to researchers in dendrochronology. Ideally, forensic investigations would be based on a range of samples obtained from trees located within and outside of the area of known or suspected contamination. This sample core was taken from a tree immediately downstream of 18 underground fuel tanks that had been installed in the 1930s and removed in the late 1980s. The core was analyzed along its length at 0.2 mm intervals with a beam size at 0.1 mm. The "spiky" series of raw EDXRF counts indicated the variability of element concentration over very short physical distances (Fig. 1). Large differences in numbers of counts among the various elements complicated the plotting of several elements on a single set of axes.

The series of raw counts of each element were smoothed using a center-weighted moving average ($\bar{C}_i$) derived from the raw counts (C) at each sampling position (i). The choice of algorithm for the moving average was intended to retain enough of the variation to detect and precisely identify changes in concentration trends while removing most of the high-frequency variation that is not readily interpretable in this study. For this example:

$$\bar{C}_i = (C_i \times 0.25) + ((C_{i_{+1}} + C_{i_{-1}}) \times 0.15) + ((C_{i_{+2}} + C_{i_{-2}}) \times 0.10 \\ + ((C_{i_{+3}} + C_{i_{-3}}) \times 0.075) + ((C_{i_{+4}} + C_{i_{-4}}) \times 0.05)$$

with the numeric subscripts referring to lagged sampling positions ahead and behind the sampling position i (Fig. 1). Due to the nature of tree-ring series, $\bar{C}_i$ values may be based on values that cross annual ring boundaries and intra-annual features such as earlywood and latewood.

Alternatively, curve smoothing may be accomplished by averaging the measurements within individual annual rings. Annualization of the series of counts is intuitively appealing as individual tree rings are a common basis of observation and calendar year provides a common expression for estimation of the timing of environmental releases. However, as annual rings vary in width, annualized means are based on a varying number of sample observations.

The annualized series were normalized as Z-scores to place the various element series on a common scale to facilitate comparison (Fig. 2). Z-scores were calculated as the quotient of the difference between the specific annual value minus the mean annual value for the entire series, divided by the standard deviation of the series. Consequently, the Z-scores have a mean of 0 and a standard deviation of 1.

Peak amounts of S, Cl, Pb, and P indicated high amplitude anomalies in wood formed in 1978. Secondary peaks of the same elements also occurred in wood formed earlier in the 1970s. Additional peaks of lesser amplitude were also present in the series, but were difficult to distinguish from the basic variability in either the raw or the annualized data. As Pb has low mobility in living wood and follows hydraulic flow, this finding likely shows that the tree was exposed to Pb

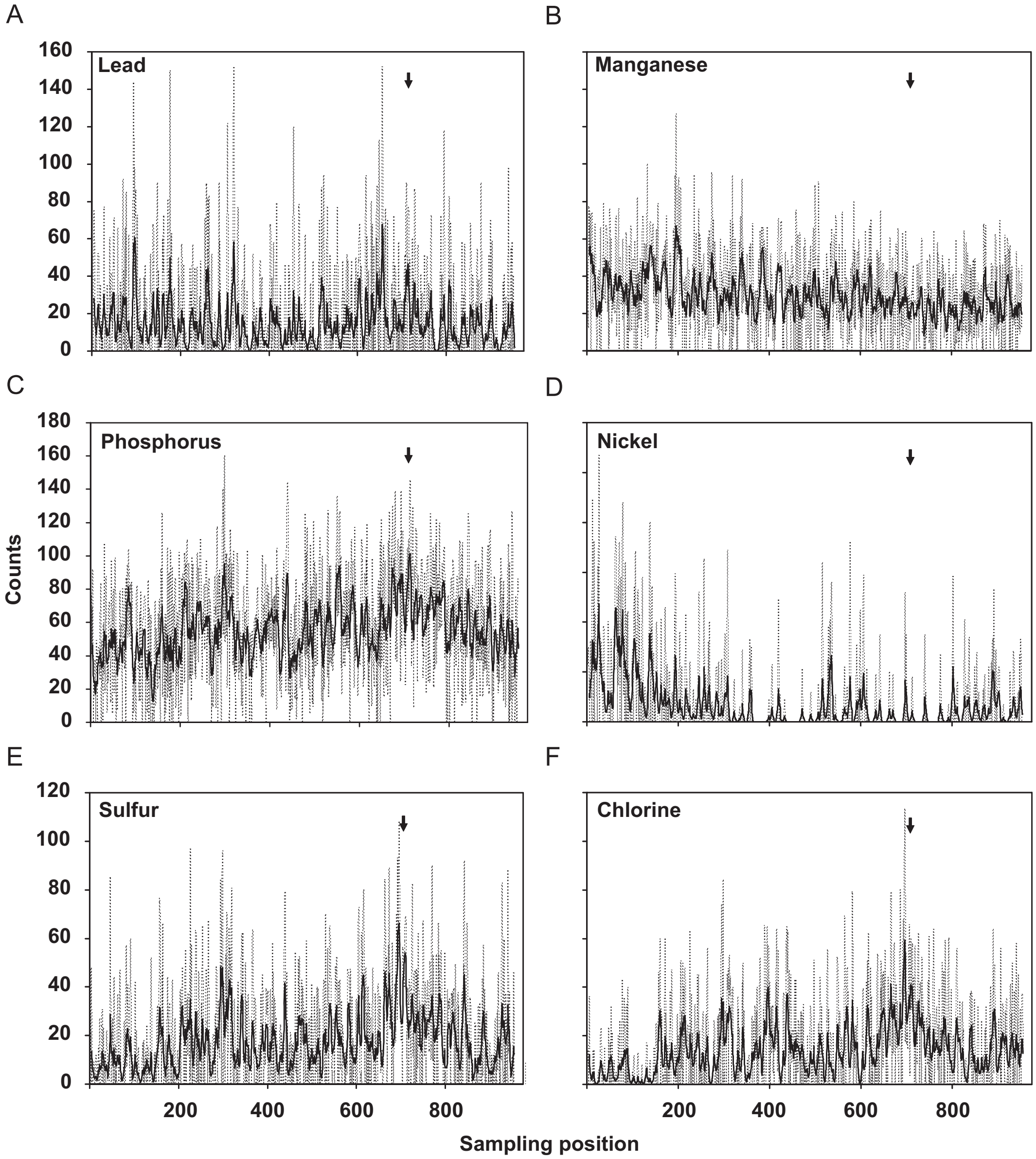

Fig. 1. Measured counts of elements derived from EDXRF analysis. A single increment core was tested of *Liriodendron tulipfera*, growing at the site of a petroleum release and that contained wood formed from 1947 to 2004. Both raw counts (dotted lines) and counts smoothed with a center-weighted moving average (heavy line) are shown. The year 1978 is marked (black arrow).

contamination in the mid-1970s. Concentration of P and S are both under some degree of active metabolic control through the translocation and cycling pathways within the tree. The soil microbial community directly affects P uptake through mycorrhizal associations (Read et al., 2004) and indirectly affects S uptake through changes in oxidation–reduction status and reduction (Rennenberg, 1999; Herschbach and Rennenberg, 2001). Additional research on the movement of elements through soil and into trees and their detection and position within tree rings is essential to reduce uncertainty and increase the utility of dendrochemistry as a research and forensic tool.

Other spectroscopic techniques such as laser-induced breakdown spectroscopy (LIBS) (Vadillo and Laserna, 2004) may also prove useful in dendrochemical assessments for environmental forensics. LIBS may have the advantage of being able to detect elements with $Z < 13$. However, the equipment is less available and has not been as frequently tested for dendrochemical applications.

Challenges in interpretation

Given an adequate chemical method, valid dendrochemical interpretation requires some understanding of

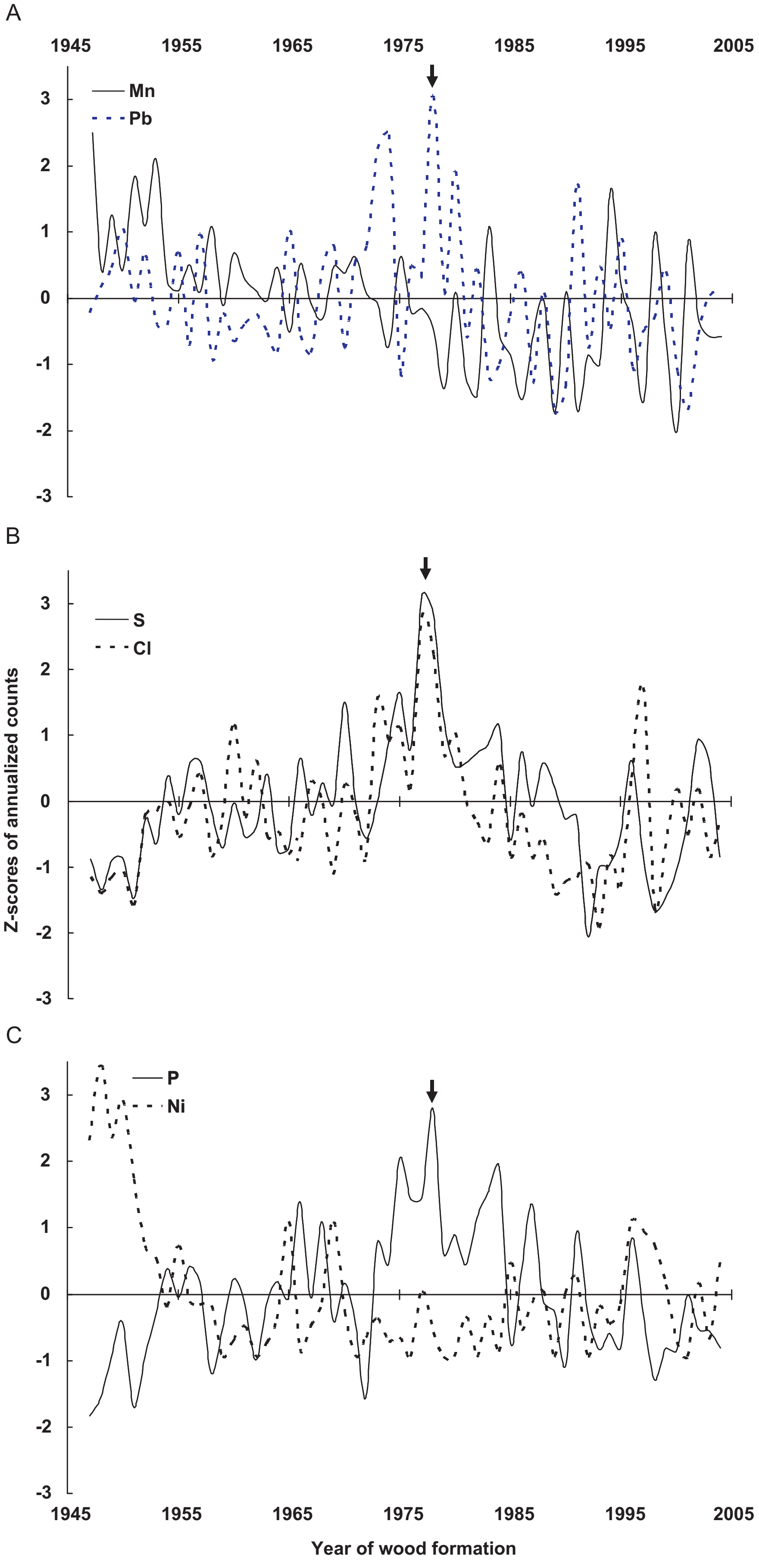

Fig. 2. Annualized departure from the mean concentration of normalized EDXRF data (Z-scores) obtained from the same core and measurement period as in Fig. 1. The year 1978 is marked (black arrow).

tree biology (Smith and Shortle, 1996) and environmental chemistry. Trees tend to maintain homeostatic concentrations of elements across a range of element availability in the soil (Smith and Shortle, 2001). Concentrations of strongly dissociated ions in the soil solution may increase during episodes of drought. This increase is less likely to occur with mineral elements more strongly bound to ion exchange sites in the soil. Moisture stress would also tend to reduce the flow of water and elements both because of reduced bulk hydraulic flow and reduced amounts of energy available for mediated uptake and translocation. Although the root system is the most frequently considered pathway for uptake, appreciable uptake of atmospherically deposited elements can occur through foliage. In herbaceous plants, foliar uptake has been demonstrated for Fe, Mn, Zn, Cu, and other elements (Kabata-Pendias, 2001).

Once within the tree, element translocation may be symplastic (through the interconnected web of living cells), apoplastic (through wood cell walls and pores), or both. Both apoplast and symplastic pathways in sapwood generally involve more than one ring, causing wood formed in past years to be exposed to active sap flow in the year of environmental impact to the tree. Translocation rates in sapwood do tend to decrease with increasing distance from the vascular cambium, but not necessarily in a linear fashion. The concentration of some elements can change in the age-related transformation of sapwood into heartwood (Meerts, 2002). The sampled *L. tulipfera* does not form heartwood. However, the inner cores of *L. tulipfera* and other trees that do not form heartwood (most frequently diffuse-porous broadleaved trees) can be altered by the tree response to injury and the development of infection within the compartmentalization boundaries (Shigo, 1984).

The frontier for dendrochemical analysis may lie in understanding enough about element uptake processes and internal processes of tree maturation (juvenile vs. adult wood), wood maturation (heartwood vs. sapwood) and infection to reasonably interpret chemical trends in wood as influenced by environmental change (Smith and Shortle, 2003).

The synchronous peaks in wood formed in 1978 are interesting in that they occurred for elements that are actively selected for (P) and actively excluded (Cl) from root uptake as well as for those that are taken up by the bulk flow of water (S) (Prenzel, 1979). Although not included in those previous investigations, Pb is likely also to be taken up by the bulk flow of water due to its relative immobility and lack of reactivity with plant tissues. This supports the concept that a record of peak exposure to an environmental release is possible, despite the homeostasis of sap chemistry (Smith and Shortle, 2001). More quantitative comparisons, particularly for elements that naturally occur in wood, may require an evaluation of uptake and translocation processes as well as comparisons of dendrochemistry with soil chemistry.

Conclusions

EDXRF can be a reliable tool for dendrochemical analysis. The cost of analysis of a sufficient number of core samples to satisfy statistical rigor may pose a challenge. Dendrochronological investigations to determine common growth trends typically compare individual rings, frequently from duplicate samples, from scores or hundreds of trees. For many sites with observed or suspected petroleum contamination, it is rare to have many trees available for core collection. The precision inherent in sampling at exact intervals of 0.1 mm along the core surface may be in stark contrast with the uncertainty introduced by the lag between the time of the contamination event, the passage of the contaminant through soil and water to the root system, and the uptake, translocation, and storage processes of the contaminant within the tree. The challenge for the investigator is to evaluate the appropriateness of available techniques to meet investigative needs within the constraints of available resources. While dendroecological and dendrochemical research requirements may differ from forensic requirements (Morgan and Bull, 2006) with respect to sample replication and statistical rigor, the practice of each may be complementary and increase the value of both types of applications.

To maximize the contribution of dendrochemistry to environmental forensics, many of these biological and inferential issues will need to be resolved. Before these considerations are completely resolved, there are opportunities for cooperative research to determine the utility and limitations of analytical techniques such as EDXRF to contribute to environmental remediation.

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