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Legal Series

Use of Dendrochronology and Dendrochemistry in Environmental Forensics: Does It Meet the *Daubert* Criteria?

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Dendrochronological methods have been in use for more than 100 years, providing us a record of climate, human activities (archaeology), floods, fire, mudslides and other geological and biological events. More recently, dendrochemisty has been used to assess the time frames of the onset and existence of environmental contamination. This article assesses the scientific status of dendrochronology and dendrochemistry with respect to the admissibility of expert testimony and *Daubert* legal criteria.
The purpose of this article is to identify the crucial scientific aspects of dendrochronology and dendrochemistry that address the *Daubert* criteria and Rule 702 as amended in 2000. To clarify terminology, *dendrochronology* is the precise and reliable assignment of the year of formation of tree rings. *Dendroecology* is the use of dendrochronology to understand ecological and environmental processes (Schweingruber, 1996). *Dendrochemistry* is a subdiscipline of dendrochronology that analyzes and interprets the wood chemistry of precisely dated tree rings. *Forensic dendrochemistry* applies dendrochemistry to resolve environmental disputes and generally deal with questions regarding the timing and/or the source of environmental incidents. One significant application of forensic dendrochemistry to expert testimony is to address issues of anthropogenic contamination. *Forensic dendroecology* is a similar term to forensic dendrochemistry, but forensic dendrochemistry will be used in this discussion as the latter term emphasizes the use of chemical detection methods. Because dendrochemistry is based on the foundation of dendrochronology, both the former specialty and the latter broader discipline will be discussed.

Keywords: dendrochronology, dendrochemistry, dendroecology, forensics, *Daubert* criteria, tree-rings

Experts often are asked to provide opinions to help resolve environmental disputes. If a dispute goes to trial, the expert's role is to provide the court with objective opinions. But how can an expert form a reliable opinion if there is debate over material evidence, analytical methods, and the interpretation of experimental results? It becomes the task of the court to assess whether or not the expert's opinion is dependable, consistent, and objective.

Attorneys for both parties scrutinize the qualification of the expert, the quality of the expertise, and potential errors or biases. Attorneys serve the best interests of their clients, whereas the experts are expected to aid the court, even though only one side in the dispute pays them. Given this allegiance by employment, an expert's views can become skewed and potentially biased (Oudijk, 2007). In criminal cases, courtroom standards such as "beyond reasonable doubt," "preponderance of the evidence," and "no material questions of fact" apply. Civil cases are different, and environmental expert opinion often comes to "more probable than not," with limitations such as: "to the best of my knowledge" or "to a reasonable degree of scientific certainty." A 100% certainty normally does not exist in science. However, in many disputes, parties eventually settle because evidence provided by one party is very strong. If the dispute is not settled, the case may go to trial and not surprisingly, opposing expert opinions often contradict one another.

Reliability of Evidence and Testimony

Admissibility of expert opinion is based on a two-step analysis in which the court determines: 1) if the expert opinion reflects scientific knowledge and is derived by the scientific method (reliability), and 2) whether the expert opinion is relevant to the task at hand (relevance). In its original form of 1975, Rule 702 of the Federal Rules of Evidence provided: "If scientific, technical, or other specialized knowledge will assist the trier of fact to understand the evidence or to determine a fact in issue, a witness qualified as an expert by knowledge, skill, experience,

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training, or education, may testify thereto in the form of an opinion or otherwise" (Ries and Burns, 2005).

In 1993, the *United States* Supreme Court issued its landmark decision in *Daubert v. Merrell Dow Pharmaceuticals, Inc.*, 509 United States (US) 579 (available online at http://www.law.cornell.edu/rules/fre/ACRule702.htm) which made significant changes in the standards for admissibility of expert opinions in federal courts. These changes included a gatekeeping requirement in Rule 104(a) under which courts must screen expert opinions for reliability and exclude 'junk science.' In *Daubert*, the Supreme Court also established a new, more flexible set of criteria for reliability and admissibility of expert opinion (Brillis et al., 2000; Ries and Burns, 2005; Kanner, 2007). According to Kanner (2007), the *Daubert* criteria include:

- the scientific technique (or "theory" applied) must be testable and verifiable;
- the technique has been published in a peer-viewed journal or other similar publication;
- the technique has a defined rate or margin of error;
- the technique is used with appropriate standards and controls; and
- the scientific community has accepted the technique or theory to a significant degree.

Requirements for reliability have been further refined since 1993 in several later Supreme Court Cases, US Court of Appeals cases, and US District Court cases. In 2000, Rule 702 was amended in response to *Daubert* and to the many cases applying *Daubert*, including *Kumho Tire Co. v. Carmichael* 526 US 137 (1999). In that revision process, additional considerations for reliability were identified:

- Whether experts are proposing to testify about matters growing naturally and directly out of research they have conducted independent of the litigation or whether they have developed their opinions expressly for purposes of testifying;
- Whether the expert has unjustifiably extrapolated from an accepted premise to an unfounded conclusion—in some cases a court may conclude that there is simply too great an analytical gap between the data and the opinion proffered;
- Whether the expert has adequately accounted for obvious alternative explanations;
- Whether the expert is being as careful as he would be in his regular professional work outside his paid litigation consulting; and
- Whether the field of expertise claimed by the expert is known to reach reliable results for the type of opinion the expert would give.

Courts applying these criteria can bar an expert from presenting testimony, which in some cases bars claims from proceeding.

In general, the science of dendrochronology clearly meets the requirements of acceptance by the scientific community. However, the acceptance of dendrochemistry by the scientific community is less clear. There has not yet been any courtroom precedent for the application of forensic dendrochemistry, the question arises as to whether or not forensic dendrochemistry meets the *Daubert* criteria.

For the first step in this admissibility analysis, the Supreme Court provided a list of non-exclusive and non-dispositive factors, characterized as "general observations," which a court should analyze in determining the reliability of scientific evidence. These factors are the five listed previously, extended to some later indicia such as those listed in 2000 amendment of rule 702.

Uses of Dendrochronological and Dendrochemical Methods

The first principle of all dendrochronological studies is that nearly all tree species in temperate forests produce a single layer of wood each year. In cross section, these layers appear as tree rings. The size, form, and chemistry of each growth ring are determined in part by the specific environmental conditions to which the tree was exposed. From this physiological basis, trees record environmental change. Biologists, climatologists, and physical geographers have used dendrochronological techniques to investigate environmental change since the turn of the past century in such diverse locations such as the arid southwestern United States, the alpine regions of Switzerland, the mountains of the Himalaya, and the harsh climate of northern Scandinavia. Since the 19th century, dendrochronological methods successfully dated and interpreted geological and hydrological conditions (Meinzer, 1927), avalanches, and rock falls (Bryant et al., 1989; Stoffel, 2006), archaeological sites and human activity (Poleski and Krapiec, 2000), climate change (Fillion et al., 1985; Carrer and Urbinati, 2004; Hamilton, 2005; Yadav, 2007; Etien et al., 2008), and hazardous flood events (Stallings, 1933).

Dendrochemistry has become a tool to measure soil and groundwater contamination from many sources and by various chemicals. For example, tree-ring studies have been used to monitor areas contaminated with arsenic (Cheng et al., 2007); fossil fuels (Baes III and Ragsdale, 1981; Balouet and Oudijk, 2006; Balouet et al., 2007; Balouet et al., 2008), heavy metals (Zou et al., 2004; Punshon et al., 2005; Devall et al., 2006; Sheppard et al., 2007), chlorinated solvents (Balouet et al., 2007; Larsen et al., 2008), nutrients (Vroblesky and Yanosky, 1990; Vroblesky et al., 1992), precipitation acidity (Kwak et al., 2008), and radioactive isotopes (Edmunds et al., 2001; Kalin, 1995; Kagawa et al., 2002; Mazeika et al., 2007; Rao et al., 2002). Tree-core studies also have been used to map the subsurface distribution of contamination by chlorinated solvents (Vroblesky et al., 1999; Schumacher et al., 2004; Vroblesky et al., 2004; Doucette et al., 2007; Graber and Soprek, 2007).

Dendrochronology, Dendrochemistry and *Daubert* Criteria

The contributions of dendrochronology to environmental forensics are based on eight widely recognized scientific principles, and three more specific ones. Given appropriate sample selection, collection, replication, and processing of tree-ring samples, the following principles have been identified:

Principle 1) Tree rings (from most trees in the temperate zones of the planet) are formed on an annual basis. This first principle has been understood for centuries, back to the days of Theophrastus (332BC) (Briand et al., 2006) and da Vinci (1956 [1651]). Some rings may however be locally absent ("missing") or false rings may form due to environmental stress (such as an unusually cold period during the growing season or defoliation by an insect pest or disease) but these anomalies can be identified through microscopic inspection, sample comparison, or cross-dating. Cross-dating is the procedure of matching ring-width variation and other structural characteristics among trees in nearby areas that allows the precise assignment of the year of formation to each ring (Fritts, 1976).

Principle 2) The width of an individual ring is determined by the interaction of internal genetics and the external environment.

Principle 3) The calendar year of wood formation in rings in a series can be accurately dated. One means of determining the ring date is by crossdating. In trees where crossdating is not practical, such as in trees with no annual-ring-width variation, trees too young to crossdate, trees growing in areas where there are no existing chronologies, or trees subject to local anthropogenic influences, the age can be determined by counting the number of rings from the bark inward. In the ring-counting method, the ring date is assigned by subtracting the number of rings, each representing a year, from the date of core collection or of tree death. The counting method must take into account the potential for missing or false rings.

Principle 4) Patterns of wide and narrow rings in tree ring series can be identified and correlated from trees growing under common environmental conditions.

Principle 5) Chronologies can be developed by aligning and cross-dating tree-ring series with different beginning and ending dates derived from living, dead, and preserved wood that extend beyond the length of extant living individuals in the component series.

Principle 6) Mechanical injuries to the living vascular cambium can be dated by the position of the wound and a tree's response to the wound within the tree-ring series (such as blazes on specific sample trees).

Principle 7) Series of tree-ring measurements of unknown dates can be dated by comparison and alignment with dated tree-ring chronologies. An exception is areas where local anthropogenic influences may overwhelm climatic signatures.

Principle 8) Patterns in tree-ring chronologies can be correlated to measured climate patterns. An exception is areas where local anthropogenic influences may overwhelm climatic signatures.

Principle 9) Climate patterns can be reconstructed from dated chronologies in the absence of direct climate measurements.

Principle 10) Chemicals present in wood samples indicate plant exposure to these chemicals. This result of plant uptake and assimilation is central to concepts such as phytoremediation (United States Environmental Protection Agency [US EPA], 2000; Pivetz, 2001) and phytoscreening (Vroblesky, 2008) where plants are used to address contamination.

Principle 11) For certain chemical elements or compounds, the date of tree exposure can be assigned or estimated from the chemical pattern in precisely dated tree-rings.

Principles 1 to 10 support the use of trees as proxy-recorders because wood accretion is influenced by environmental perturbations, such as climate, disease, or contamination. Principles 1 to 4 are supported by an estimated 10,000 publications. Many of these publications have been archived and can be readily accessed online at http://www.wsl.cldbdendreindex_EN?redir-1& (Grissino-Mayer, 2009) while Internet search engines such as Google provide 40 million entries to "tree-rings" and 38,000 to "dendrochronology"). By comparison, Principles 5 to 7 may be supported by an estimated thousand publications, while principles 8 through 9 are backed up by several hundreds of publications. Principle 10 is a more recent development and started about 5 decades ago. It is backed up by an estimated 300 publications (Chiment and Chiment, 2005). Selected publications supporting principle 10 are cited in the following sections.

History of Past Uses of Trees as Witness Trees or Proxy-Recorders

During the 19th century there was much debate concerning the use of tree rings to determine the age of trees (Briand et al., 2006). Trees were often used as property markers (known as "witness trees") and their age was important in boundary disputes. In an 1830 case from Maryland, a judge ruled that tree rings were not representative of a tree's age. However, by the 1850s the science had improved and it became accepted within the American legal system that each ring represented one year. Tree-ring studies then became an acceptable means to date trees. Featherly (1956) provided a description of five cases where tree-ring studies were accepted by courts in the United States. These five trials took place between the 1920s and 1940s and four of the five dealt with environmental events. One 1941 trial from Oklahoma dealt with contaminated water originating from petroleum development. Featherly also recalls the successful use of dendrological methods in a major criminal case, the kidnapping of Lindbergh's child.

Significant advances began in dendrochronological theory at the turn of the last century. Archaeological research in Arizona and New Mexico of the southwestern United States spurred the use of these methods (Douglass, 1933; Nash, 1999). Later in the century it was found that past climates could be reconstructed through tree-ring studies (Fritts, 1976). By the 1970s, tree-ring studies were being used to reconstruct the nature and timing of geological and environmental events such as avalanches, fires, landslides, floods, tree diseases, and so forth. The provincial government of British Columbia in Canada recently published a guide to the dendrochronological analysis with respect to hydrological events (Wilford et al., 2005).

From the 1980s, dendrochronology has been used to date environmental contamination through changes in growth patterns. The question now is: Can forensic dendrochemistry meet the *Daubert* criteria and its progeny for admissibility of expert opinion to resolve environmental disputes?

Have Dendrochronology and Forensic Dendrochemistry Been Thoroughly Tested?

Chronologies have been established for thousands of trees worldwide (probably more than 10,000) and have been used to establish past climates and age-date fire events, insect plagues, and floods. Additionally, dendrochronologists have developed pertinent methods to cross-date and check on chronologies.

The testing of dendrochemistry, *senso stricto*, refers to those specific cases where both pollutant species and release timeframe were precisely known prior to dendrochemical investigation, or where the dates were confirmed by alternative methods. Sheppard and Funk (1975) correlated in tree-rings the uptake of heavy metals at concentration profiles matching in time the mining activity in Coeur d'Alene, Idaho. Baes and Ragsdale (1981) and Watmough et al. (1998), correlated increases in traffic to the quantity of lead in the rings of nearby trees. They were also able to correlate in time the introduction of lead in gasoline through the lead content in tree rings. Vroblesky and Yanosky (1990) confirmed the presence and timing of contaminants in tree-rings they studied using historical refuse records at a landfill site in Maryland. The US National Climatic Center http://www.ncdc.noaa.gov/paleo/hurricane/references.html lists 19 dendrochronology-based publications in its paleotempestology page, 3 of which are based on dendrochemistry, including isotopes (Latimer et al., 1996; Oberbauer et al., 1997; Reams and Van Deusen, 1996) that support the age-dating of past well documented tornado events.

Rao et al. (2002) observed radioactive contaminants in Japanese tree rings and correlated these elevated concentrations to the 1945 atomic-bomb explosions. In 2003, Punshon et al. (2003, 2005) presented a study on a nickel (Ni) release from a former radiological settling basin after an enclosing spillway breached in 1984. The dendrochemical signal was associated in time with the release of Ni and other heavy-metal co-tracers such as copper (Cu), zinc (Zn) and chromium (Cr). Pearson et al. (2005) tested the use of forensic dendrochemistry to the age-dating of volcanic eruptions, including on well documented events. Balouet et al. (2007) presented a litigated case study in which the dating of release and spread of chlorinated solvent plume was precisely corroborated by technical documents on leak and repair activity. Sheppard et al. (2008) provided a similar confirmation of a dendrochemical signal for sulfur (S) and phosphorus (P), associated with the 1943 volcanic eruption of Paricutin, Mexico. Abreu et al. (2008) confirmed the synchronous dendrochemical uptake of anthropogenic mercury released by a chlor-alkali plant in Portugal.

In the above thirteen examples, release time frames were known and historical markers were present, i.e., documented leak and repair at an industrial facility, a refuse record at landfill, the 1945 atomic-bomb explosion in Japan, the 1923 introduction of leaded gasoline in the United States, chlor-alkali plant or mining activities, dam failure, volcanic eruptions, and tornadoes were all detectable in the dendrochemical record in Europe, Central and North America, Japan. In each of the above cases, the analytical equipment did differ.

If forensic dendrochemistry is reliable enough for the 13 tests noted previously that were reliably dated using other corroborative evidence, then forensic dendrochemistry is scientifically sound enough to be used for legal issues. Forensics dendrochemistry has otherwise been used to check on the existence of datable signals in tree rings, where release sources were known, but the exact time frame was not (Balouet et al., 2007, 2008). Dendrochemical signals for environmental releases associated to several compounds can also be used to test the timing and nature of pollutant releases (Punshon and al., 2003; Sheppard et al., 2008).

Has Dendrochronology and Forensic Dendrochemistry Been Subjected to Peer Review and Publication?

There are on the order of 10,000 publications that use dendrochronological methods in peer-reviewed journals devoted to natural environmental records such as *Dendrochronologia* and *Geochronometria*, or more general peer-reviewed scientific journals such as *Environmental Forensics*, *Journal of Environmental Quality*, *Ground Water* and *Environmental Science and Technology* (Balouet, 2005). The scientific community has accepted the use of dendrochronology to interpret environmental events. Based on the presence of peer-reviewed articles as early as the 1930s, this acceptance has been in place for more than six decades.

Peer-reviewed publications of applications where forensic dendrochemical concentrations were reported to be reliable indicators of environmental change of precisely dated events include Baes and McLaughlin (1984), Baes and Ragsdale (1981), Balouet et al. (2007; 2008), Bondietti et al. (1990), Guyette and

Cutter (1994), Momoshima and Bondietti (1990), Orlandi et al. (2002), Pearson et al. (2005), Punshon et al. (2003), Sheppard et al. (2008), Rao et al. (2002), Vroblesky and Yanosky (1990), Watmough et al. (1998), and Yanosky and Kappel (1997).

Several peer-reviewed publications dealt with the use of forensics dendrochemistry, *senso lato*, to age-date environmental releases where the contaminants' chemistry was known, but release time frame was not. In such cases, identification of the contaminant signal in trees typically is based on finding an accumulation of a target chemical, representative of the investigated environmental event, in synchronous growth rings from multiple trees in the affected area (Pearson et al., 2005). The correlation between dendrochemistry and the investigated environmental event can be further strengthened by ensuring that synchronous accumulation of a target chemical was not found in nearby background trees. In addition, the use of multiple tracers sometimes can clarify the source of the target chemical in trees. For example, Balouet et al. (2007, 2008) found that high concentrations of chlorine (Cl) in growth rings could indicate impact from chlorinated solvents if Cl were the only elevated constituent, and could also indicate impact from road salt if Cl, calcium (Ca), P, and potassium (K) were correspondingly high. Similarly, synchronous elevation of S, Cl, and lead (Pb) can be used to indicate impact from leaded gasoline. A similar approach was used by Punshon et al. (2003) for relating a dendrochemical signal to the 1984 dam failure in the vicinity of a radioactive settlement basin.

Does Forensic Dendrochemistry Have Any Known or Potential Rate of Error?

All data accumulated in field studies contain degrees of error due to both sampling and analysis (Miesch, 1967). Potential errors associated with dendrochemistry involve aspects related to dating (traditional dendrochronology) and aspects related to behavior of the chemical species in the wood. In general, the margin of error for dendrochronological dating is one tree ring or one year, which often is adequate for forensic investigations. Occasionally, in tree cores where the growth rings are small, multiple growth rings can be combined for a single analysis, making the margin of error equal in years to the number of growth rings that were combined. Potential errors associated with dendrochemistry are more complex and depend on a variety of factors, including the type of chemical and the movement of the chemical in the tree.

Although dendrochronology usually is accurate to approximately 1 year, limitations sometimes may cause the age-dating precision for individual rings to range over more than one year. For example, missing rings or extra rings can occur. If a very cold summer was to occur, a ring may not be discernible. On the other hand, if a significant cold spell happened during the summer, two rings could be recorded in 1 year. To determine if such anomalies exist, researchers need to broaden their own sampling and/or consult available archives, such as the International Tree-Ring Data Bank (ITRDB), operated and maintained by the NOAA Paleoclimatology Program and World Data Center for Paleoclimatology. The ITRDB contains tree-ring chronologies derived from many series obtained from numerous tree species and locations. Diligent application of the dendrochronological technique of cross-dating (Fritts, 1976) can detect and account for locally absent and false rings. Software programs such as "Cofecha" can also help identify potential problem areas during the cross-dating of tree-ring series and chronologies (Grissino-Mayer, 2001).

Some level of error in the assignment of the date of tree exposure to environmental chemicals can be associated with dendrochemical investigations. In some tree species, sap is conducted through more than the most-recently-formed growth ring. This can result in the exposure of tree rings prior to the environmental release of the contaminant marker (Smith and Shortle, 1996; Smith et al., 2008). This phenomenon is seen in analysis of tree-rings for "bomb isotopes" (such as tritium) (Bondietti et al., 1990; Smith and Shortle, 1996). This aspect of elementary tree physiology is often the source of confusion and misleads some investigators to attribute such patterns as chemical translocation across tree rings. Although translocation along the trunk radius does occur in some species, particularly with the transformation of sapwood into heartwood, identification of those compounds often can be determined in site-specific applications by comparing ring chemistry to heartwood/sapwood relations. Within the *xylem*, studies indicate that: arsenic (As), sodium (Na), and magnesium (Mg) appear to have relatively high mobility between active tree-rings; strontium (Sr), Ca, Zn, Cu, and Cr appear to have moderate mobility; barium (Ba), aluminum (Al) and cadmium (Cd) appear to have relatively low mobility (Cutter and Guyette, 1993; Prohaska et al., 1998; Padilla et al., 2002); and translocation of Pb in conifers was minor and likely impacted the tree at the time the ring was formed (Devall et al., 2006).

Lead and sulfur are elemental markers that can be helpful in forensic studies, such as estimating the time frame of fossil fuel releases (Balouet et al., 2007). Lead, in the form of tetraethyl lead and tetramethyl lead, was added to automotive and aviation gasoline from 1923 to 1996 in the United States. Sulfur continues to be present in middle-distillate fuels such as motor diesel fuel, jet fuels, and heating oils. Dendrochemistry studies using S as pollution marker have been applied to study atmospheric pollution (Watmough et al., 1998) and age-date volcanic eruptions (Sheppard et al., 2008). Fairchild et al. (2009) further showed that tree rings older than a few years, contain an archive-quality record of sulfur exposure. Of significant relevance to releases of chlorinated solvents is chlorine. Cl does not appear to cross growth ring boundaries based on most studies (Vroblesky and Yanosky, 1990; Yanosky and Kappel, 1997; Hagemeyer, 1995). One study, however, found that there was reverse translocation of Cl in bald cypress trees impacted heavily by salt-water intrusion and concluded that it was a survival adaptation by this salt-tolerant species to periodic saline flooding (Yanosky et al., 1995). The apparent difference appears related to tree species.

In practice, concentrations in tree rings of chemicals known to be constituents of the target contamination and known to be relatively immobile across growth-ring boundaries potentially can be viable forensic evidence if there are anomalous patterns that significantly differ from patterns of the same chemicals in nearby background trees of the same species. With respect to chemical fingerprinting, the chemical characterization of pollutant's composition, the analytical methods to determine wood chemistry will have ranges of error inherent to the analytical equipment used. Error ranges for laboratory chemical analyses are normally between 1% and 5%, or higher with some methods. The laboratories that perform these functions should be consulted for specific values. Forensic investigators, as explained in Balouet and Oudijk (2006), Balouet et al. (2007, 2008), and Smith et al. (2008), must acknowledge and account for such limitations. Despite these limitations, dendroecological evidence can be used effectively to estimate time ranges of plume development and tree exposure.

Does Forensic Dendrochemistry Have and Maintain Standards Controlling the Technique's Operation?

Numerous textbooks have been published on dendrochronology techniques and these publications provide guidelines on how to perform tree-ring studies (Fritts, 1976; Cook and Kairiukstis, 1990; Schweingruber, 1996; Nash, 1999). Dendrochronology is taught in graduate level courses at several schools such as the University of Arizona (Tucson, AZ), Columbia University (New York, NY), and the Swiss Federal Institute for Forest, Snow and Landscape Research (Berne, Switzerland). Accordingly, there are numerous sources to consult to determine how the scientific community performs such investigations and whether or not a forensic-dendrochronological investigation conformed to established protocols. Several institutions have produced guidelines on how to analyze wood collected from living trees to test for exposure for environmental contaminants. The United States Geological Survey recently published a guide on how to assess volatile-organic contamination of soil and groundwater from chemical analysis of tree cores (Vroblesky, 2008). These guides provide recommendations on sampling methodologies, sample preservation and laboratory analytical techniques.

These dendrochronology and phytoscreening efforts are necessary supports, but do not directly address the need to apply and maintain uniform standards for dendrochemical analysis. Currently, various laboratories are using different testing methods for analysis and interpretation. Most of the analytical equipment used in dendrochemistry, such as GC/MS (Gas Chromatography/Mass Spectrometry), GC/FID (Gas Chromatography/Flame Ionization Detection), XRF (X-Ray Fluorescence) laser ablation ICP-MS (inductively conpled plasma mass spectrometry) however comply with industry standards, such as set by American Standard for Technology and Materials (ASTM) or U. S. Environmental Protection Agency (EPA) approved methods. The various methods are not yet resolved, and current research will likely contribute to the emergence of preferred analytical methods, out of those already in use, or lead to "dendrochemistry standard methods."

Has Forensic Dendrochemistry Been Accepted by the Scientific Community?

The scientific community has accepted dendrochronological techniques to date tree rings and to relate anatomical characteristics of tree rings to environmental causes. In contrast, studies of dendrochemistry have been the subject of greater debate. While several studies found that dendrochemical concentration changes were reliable indicators of environmental change through time (Baes and McLaughlin, 1984; Momoshima and Bondietti, 1990; Bondietti et al., 1990; Guyette and Cutter, 1994; Yanosky and Kappel, 1997; Orlandi et al., 2002; Punshon et al., 2003, 2004; Pearson et al., 2008), other studies found no correlation (Hagemeyer, 1993; 1995; Hagemeyer et al., 1992; 1994; DeWalle et al., 1999; Bindler et al., 2004). Studies that found no correlation with environmental changes either concluded that the method was not useful to date the target event or attributed the dendrochemical changes to differences in the nature of heartwood and sapwood (Brownridge, 1984), to element accumulation in the outermost rings (Poulson et al., 1995), to radial transport and water transport through multiple sapwood rings (Lukaszewski et al., 1988; Hagemeyer et al., 1994; Zayed et al., 1992), or to reliance on analytical approaches that homogenize the wood (Brabander et al., 1999). The apparent controversy illustrates the need to understand the influences on dendrochemistry when interpreting the data. With a proper understanding of the influences, researchers can avoid reliance on particular tree species or tracer-elements that laterally translocate across ring boundaries and across the heartwood/sapwood interface and elements that can accumulate in the outermost rings, such as potassium. Knowledge of the types of trees that move water through multiple growth rings can allow researchers utilizing those tree species to assign a broader range of age uncertainty to a dendrochemical anomaly. Furthermore, analytical methodology has improved over time, reducing the need to analyze cores by homogenizing multiple growth rings. In addition, it is important to understand that there will be some situations in which dendrochemistry does not preserve a record of the target event. This can be illustrated for S and Cl in trees near the seashore where the natural background concentrations are very high. Thus, despite admitted limitations over forensic dendrochemistry, it is probable that the pit-falls associated with some of the negative studies can be avoided and that dendrochemistry has the potential to function as effective admissible evidence in legal proceedings and can provide a scientifically-defensible record of historical environmental events.

Do Dendrochronology and Forensics Dendrochemistry Meet Other Indicia of Reliability?

Two major indicia of reliability are the extent to which the method or theory has been used as a scientific tool outside of litigation and its use in litigation. Dendrochronology has been used in thousands of research studies in climatology, ecology, art history, and archeology by a diverse community of scientists. It has also been used in dozens of litigated cases, usually concerning historical remains or art work, the majority of which were settled out of court. Where it has been used in litigation, the same techniques have used as in studies that did not involve litigation. The only case that we found for which dendrochronological evidence was proposed and then discarded was from the 19th Century case referred to by Briand et al., 2006.

Dendrochemistry has been used to estimate the timing of environmental impacts in dozens of instances outside of litigated cases (see section 1 on tests). The mobility of As across tree rings was excluded in at least one case in South America. Dendrochemical evidence was presented in over 2 dozen cases that were settled prior to trial and at the time of this writing is being submitted in two distinct US Court cases that have not yet been litigated. The same techniques have been used in litigation as in the other instances.

Other indicia of legal admissibility do address sample quality, adequacy of analytical equipment and procedures, and alternative explanations for findings. In all litigation cases, the reliability of experts and their testimony are screened by attorneys and Courts to assure that experts are qualified with respect to skill and experience. The authors do not know of any litigated case in which other factors had been used to support or disqualify admissibility. In this paper we present the current scientific knowledge, applications, and potential limitations with the understanding that this is an active area of investigation and subject to new discoveries.

Conclusions

Scientific practitioners all over the world have used dendrochronological methods for more than 100 years. Over the past three decades dendrochemistry has been used to fingerprint and date environmental contamination. In addition to the cases the authors have worked on, and settled out of court, results from some most pertinent cases litigated are still confidential. The proper use, in the judicial system, of historical records derived from dendrochemistry requires a thorough understanding of the scientific processes and discussion of the limitations associated with the methods.

This article compared each of the five *Daubert* criteria to what is known about forensic dendrochronology and dendrochemistry. The *Daubert* criteria have been met for dendrochronology. For dendrochemistry, as with other forensic methods, there are dozens of consistent cases and published studies that positively support the method, but with limitations.

These limitations include the proper evaluation of analytical and ring dating margin of error, sample quality as for possible alternative causes to dendrochemical anomalies; proper use of controls, excluding some specific environments where searched tracers are naturally enriched, taking into account pollutants' stability, versus mobility within tree rings. However, the previous limitations, in the opinion of these authors, should not be used to discard the method but highlight the need for careful investigation and presentation. Future research will clarify and strengthen possible forensic interpretations and legal admissibility. Forensic dendrochemistry is a promising method and is based on a definitely accepted set of scientific methods, where standards and controls exist. Dendrochronology and forensics dendrochemistry can be used as an independent line of evidence or as part of a multidisciplinary approach, and can be used effectively to resolve many environmental disputes.

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