Dendrochemical Findings for Pinus Nigra Trees Grown in the Mediterranean Region

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Service Provided: Penn State Breazeale Reactor, Neutron Activation Analysis, Radionuclear Applications Laboratory

Sponsors: The Penn State Radiation Science and Engineering Center, Cornell University Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology

Introduction

The aim of this study was to analyze elemental constituents of tree-ring samples from *Pinus nigra* trees grown in the Mediterranean region. It has been previously shown that elemental concentrations in tree-rings may be correlated with significant chemical changes in the soil environment, such as fallout from volcanic ash and acid rain [1][2][3][4]. Establishing whether a group of trees is sensitive to these changes in the soil conditions and registers them in the elemental chemistry of contemporary growth rings is the fundamental goal of dendrochemical research. Short-term climatic perturbations (1-3 years) linked with volcanic sulfur in the stratosphere and ash fallout and subsequent acid rain may cause growth anomalies and elemental uptake/deposition rate changes in the trees. In this study, elemental weight fractions were measured in tree-ring samples using Neutron Activation Analysis (NAA) at the Pennsylvania State University (PSU) Radiation Science and Engineering Center (RSEC) in tree-ring samples of eleven absolutely dated modern forest trees. Sample trees were collected and dated by the Malcolm and Carolyn Wiener Laboratory for Aegean and Near Eastern Dendrochronology at Cornell University. The last tree-ring under the bark of the sampled trees was formed in the year in which the field collection was made. Therefore, from this known starting point, with absolute certainty, the combined time-series for the site were absolutely dated.

Two different analysis methods of NAA were used; the well-known k_0 method and a novel technique developed previously, called the Multi-isotope Iterative Westcott (MIW) method [5], [6]. The MIW method uses reaction rate probabilities for a group of isotopes, which can be calculated by a neutronic simulation or measured by experimentation, and determines the representative values for the neutron flux and neutron flux characterization parameters based on the Westcott convention. Elemental weight fractions of standard reference material and tree-ring samples were then calculated using the MIW and k_0 analysis methods of the NAA and the results were cross-verified.

Detailed investigations of the sampled species' physiology, growing environment, soil properties and nearby pollution sources were conducted previously [6]. To prevent mold, tree-ring samples were stored in a dry environment. For each tree-ring, two new razors were used to clean the surfaces and to dissect the tree-ring under an optical microscope. Sample bags were pre-weighed and wood weights were calculated by weighing the filled bags before activation. Tree-ring samples were loaded into irradiation vials as shown in Figure 1 and irradiated in dry tubes (DT-1 and DT-2) of the Penn State Breazeale Reactor. Tree-ring samples were irradiated, handled, and measured almost identically according to written procedures [6].

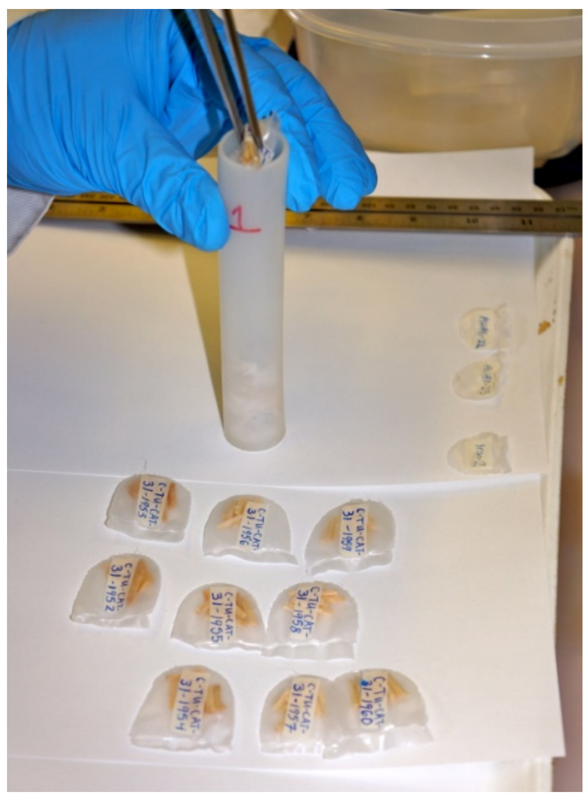

FIGURE 1: Tree ring samples are loaded into irradiation vials

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Results

In total, 27 elements have been identified in analyzed tree-ring samples, including: Na, K, Sc, Ca, Cr, Mn, Cu, Fe, Co, Zn, Ga, As, Br, Rb, Mo, Ag, Sb, Cd, Ba, La, Eu, Sm, W, Hg, Au, Ce and Se. Fourteen elements (Na, K, Ca, Mn, Zn, Br, As, Ag, Cd, Ba, La, Eu, Sm and Au) have been mostly continuously identified in tree-ring sequences. Other elements were identified in scattered rings.

An example of positive correlations between elements Sc, As, La and Sm in one of the trees (C-TU-CAT-21) are shown in Figure 2. If an environmental event has affected the trees, this should appear as a correlated concentration peak among all or at least the majority of the trees. Elemental concentrations of each element have been compared to identify such concurrent concentration irregularities across the sampled trees. For example, in six out of ten trees, Zn concentrations were found to be correlated, as shown in Figure 3. Also shown in Figure 3, however, the Zn concentrations do not lead to any correlated concentration spikes (peaks) among the majority of the trees.

In all trees but one, Br concentration in tree-ring samples from 1970-1980 onwards was found to increase. Although this increase may look like an environmental signal, it may well be associated with the internal physiology and age of the tree samples. The trees may be transferring this toxic element through their phloem to the non-living tissue, bark [7]. Br is a chemically active element with high mobility in most environments and can form salts and organobromine compounds [8], [9]. Br is used in industry and agriculture, and the world production for Br continuously increases [9]. It is not known why plants accumulate Br nor its role in plants [9]. Normalized Br concentration in one of the sampled trees (CAT-27) is plotted with 1 σ error bars (measurement uncertainty) in Figure 4. The sapwood boundary for CAT-27 was around tree-ring 1942.

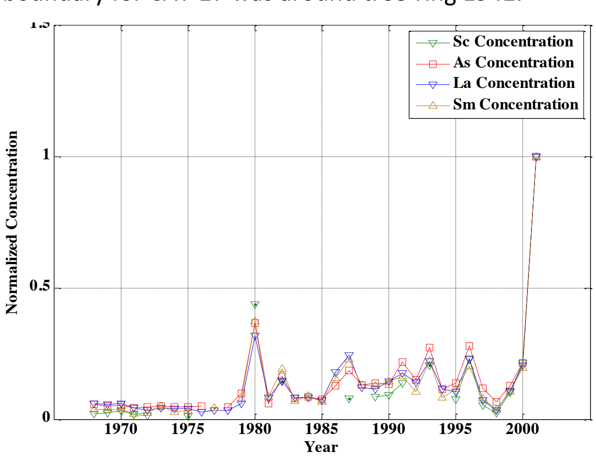

Figure 2: Normalized Sc, As, La and Sm concentrations in CAT-21 tree-ring samples.

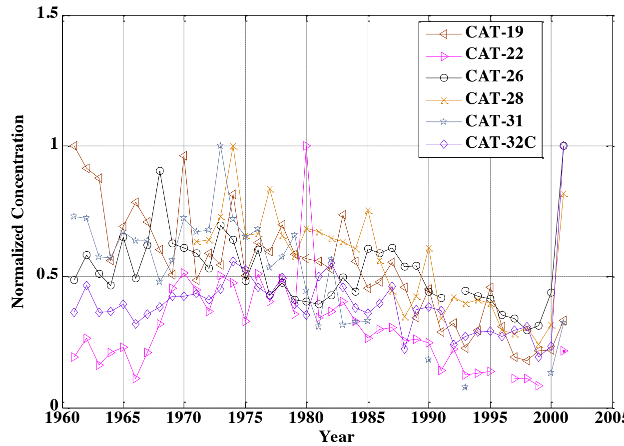

Figure 3: Normalized Zn concentration in CAT-19, CAT-22, CAT-26, CAT-28, CAT-31 and CAT-32C.

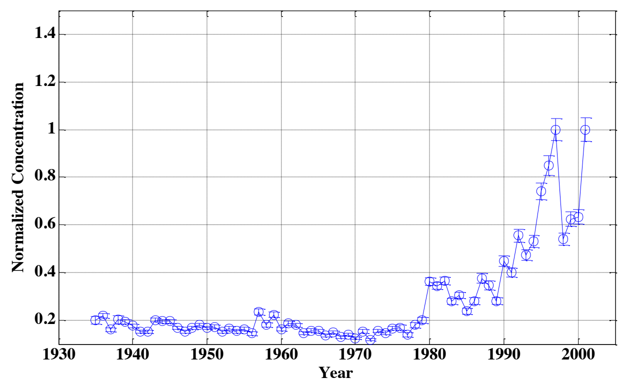

Figure 4: Normalized Br Concentration in one of the sampled trees (CAT-27) with 1 σ error bars

Uncorrelated behaviors of elemental concentrations observed for the majority of the trees. These uncorrelated concentration changes were expected, and they were related to inter-tree variability, such as the local soil properties, insect or animal attacks and internal physiological conditions that affect each individual tree.

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