X-ray Based Tree Ring Analyses

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Abstract

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In this thesis, two x-ray based dendro-analyses (batch-wise microdensitometry and energy dispersive x-ray fluorescence (EDXRF)) and the conditions under which these methods could be used on the two typical boreal conifers Norway spruce (*Picea abies* (L.) Karst.) and Scots pine (*Pinus sylvestris* L.) were evaluated. For density measurements using batch scanning x-ray densitometry, sample preparation and density calibration are vital to acquire high resolution and precision in densitometric measurements. Thickness and alignment should be adapted to give optimal resolution without loss of precision. Samples should be extracted to remove resins before wood density measurements. Ca, Mn, Fe, and Sr and in most cases K and Zn could thus be measured in an efficient way using EDXRF. Significant differences in concentrations between tree rings were found for all of these elements except Sr, indicating that tree ring concentrations of these elements could be correlated to changes in the tree environment. For Mn a correlation between soil pH and Mn concentration in tree rings was found. Other correlations between tree ring element concentration and tree environmental factors were also found. For most elements in tree-rings of Scots pine and Norway spruce it seems that the concentration is due to environmental conditions during the year the tree-ring was developed and several years afterwards. It is concluded that microdensitometry and EDXRF analyses on increment cores are cost-efficient and non-destructive analyses of wood properties. Batch-wise, x-ray based dendrochemical analysis provides opportunities for more property-based use of wood raw material and for environmental monitoring.

Keywords: trace element, trace metal, dendro analysis, dendroecology, annual ring, growth ring.

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Appendix

Papers I-V

The present thesis is based on the following papers, which will be referred to by their Roman numerals:

I. Bergsten, U., Lindeberg, J., Rindby, A. & Evans, R. 2001. Batch measurements of wood density on intact or prepared drill cores using x-ray microdensitometry. Wood Sciences and Technology 35, 435-452.
II. Lindeberg, J. Dendrochemical Analysis Based on X-ray Fluorescence. (Manuscript)
III. Lindeberg, J., Enqvist, J. & Bergsten, U. EDXRF Analysis of Metal Content in Spruce Trees. (Manuscript)
IV. Lindeberg, J. Variation in Trace Element Concentrations Between Tree Rings in Scots Pine. (Manuscript)
V. Lindeberg, J. & Enqvist, J. Soil Chemistry and Tree Ring Element Concentrations in Scots Pine. (Manuscript)

Introduction

Wood properties in trees are influenced by environmental conditions, e.g., water, nutrients, temperature, light, and ground conditions (Creber & Chaloner 1984). These conditions vary both temporally and spatially and may also partly be controlled by foresters. In this way variability in wood properties between stands, between trees, and within trees are created. This high variability in wood properties can be found in most tree species (Zobel & van Buijtenen 1989).

Wood is used in many ways and the quality criterions of the wood raw material differ for the production of different end products. However, all quality criterions are based on basic wood properties – wood anatomy, fiber/tracheid morphology, and chemical composition. It should therefore be possible to utilize the high variability by sorting wood accordingly to these basic wood properties and thereby achieve higher quality in the wood raw material delivered to different producers. As foresters may influence the environment and thereby wood properties a higher wood quality could also be achieved by silvicultural activities. To affect wood properties by silviculture and sort wood for different wood properties in an efficient way, more knowledge about the relations between environmental conditions and wood properties for different tree species is needed. To gain this knowledge a first prerequisite is to have efficient and reliable methods and techniques for measuring different basic wood properties.

The fact that a tree's environment influences wood properties allows access to information about the environment by examining wood properties. Therefore, trees could act as environmental markers revealing information about their environment. Because many wood properties are developed at the time wood is formed, trees can be used as historical archives for their environment. Ring properties – ring width, density, and trace element content – has been used for dendroecological studies including correlation with environmental pollution and reconstruction of stand history, fire history, and climate (Fritts & Swetnam 1989).

The use of x-rays to reveal wood properties is increasing. A major feature that makes x-ray measurements appealing is its non-destructive nature on wood. Two relatively easy applications and cost-effective methods using x-rays are microdensitometry and energy dispersive x-ray fluorescent spectrometry (EDXRF). Because most wood properties are more or less correlated to several other properties, these two measurements provide information other than just density and trace element variations. It is, for example, possible to identify juvenile wood (Sauter *et al*. 1999), early/late wood proportions, and compression wood (Seth & Jain 1978) from density measurements. In addition, compression wood is also related to large variations in trace element content (Prohaska *et al*. 1998). This type of information facilitates and improves the ability to predict other properties. To further improve the applicability of these methods, it is necessary to find techniques that enable measurements to be performed with high resolution in wood. Often tree rings are only fractions of a millimeter in size and some properties such as latewood density are confined only to parts of the rings. Another important factor to consider in dendro analysis is the need for cost-

effective and less time-consuming analyses to enable the use of large samples. This includes the whole chain from sampling through sample preparation and measurements to analysis of measurement data. It is well known that there is a large variation within an annual ring in trees and between trees within the same stands (Vimmerstedt & McClenahen 1995; Prohaska *et al*. 1998), and large samples are needed to evaluate relationships between external factors and wood properties. It is also important to have high precision in measurements to keep sample sizes down.

X-ray interactions with wood

X-rays are defined as electromagnetic radiation with a wavelength between approximately 10^{-3} nm (1.24 MeV) and 10 nm (124 eV). In spectrometry, it is more common to treat radiation in terms of photons instead of wavelengths. The type of interactions occurring between the atoms and molecules in matter and electromagnetic radiation are dependent on the photon energy. In the energy range of x-ray radiation, electrons dominate interactions. This can roughly be explained by the photons having approximately the equivalent energy as the binding energy for electrons within atoms. There are mainly three different types of interactions between x-ray radiation and electrons: (1) photoelectric absorption where photons use up their energy to eject electrons; (2) coherent scattering where the photons are scattered after interactions with electrons without losing energy; (3) incoherent scattering where photons lose some of their energy being scattered from interactions with electrons. These interactions are usually described in terms of probabilities, which differ with the energy of the radiation and the atomic numbers of the atoms it interacts with.

In x-ray densitometry, the densities are measured by irradiating a sample with x-radiation and detecting the amount of radiation that is transmitted through the sample. The transmission of radiation depends on how much radiation is attenuated in the sample. The probability for attenuation is the sum of the probabilities of interactions mentioned above. This can be described with the following formula according to Beers law, where I is the transmitted radiation, I_0 is the intensity of the radiation entering the sample, μ is the attenuation coefficient describing the probability of attenuation, ρ is the density of the sample, and t is the sample thickness:

$$I = I_0 \cdot e^{-\mu \rho t}$$

Analysis of trace element content in wood by x-ray fluorescence is based on the fact that electrons within an atom are bound to the nucleus with different binding energies. These binding energies are fixed to certain energy levels. Accordingly, the electrons are in different shells (K, L, M, and so on) and further into sub-shells (e.g. L1, L2, L3). The electrons closest to the nucleus have the highest binding energies and higher atomic numbers indicate higher binding energies in each shell. When a photon is photoelectrically absorbed, an electron is ejected and thereafter replaced with another electron with lower binding energy, i.e., from an electron shell further out from the nucleus (Fig. 1). The electron loses energy corresponding to the difference between the two levels of binding energy and

produces a photon of fluorescent radiation corresponding to this energy loss. Obviously there are several possible combinations of energy levels for the ejected and replacing electrons to originate from, resulting in several possible energies for the fluorescent radiation.

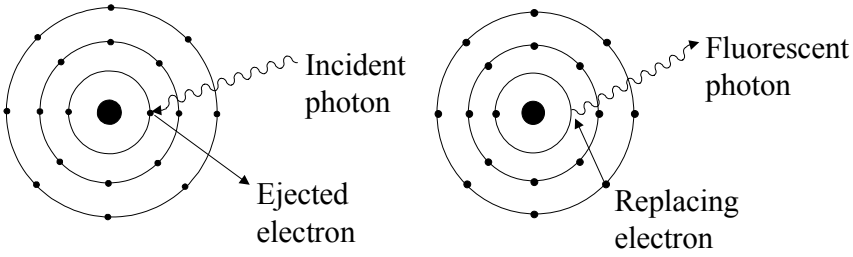

Fig. 1. Photoelectric absorption of a photon followed by the formation of a fluorescent photon.

The probability for photoelectric absorption of an incident photon by an atom (τ) is the sum of probabilities for electrons from different energy levels to absorb photons ($\tau = \tau_K + \tau_{L1} + \tau_{L2} + \ldots$). These photoelectric absorption probabilities depend on the energy of the incident radiation, and if this energy does not exceed the binding energy, the probability is zero. After the ejection of an electron, each possible transition (e.g., the K-L3 transition where an ejected K shell electron is replaced by a L3 shell electron) has a relative probability (e.g., $f_{K\text{-}L3}$) of which the total sum is one (e.g., $1 = f_{K\text{-}L3} + f_{K\text{-}L2} + f_{K\text{-}M3} + \ldots$). There is also a chance for a fluorescent photon to be photoelectrically absorbed on its way out of the atom and the probability of a fluorescent photon to escape from an atom is denoted as fluorescent yield (e.g., $\omega_{K\text{-}L3}$). The probability for a fluorescent radiated photon with a specific energy from an atom caused by an incident photon can thereby be calculated using the following equation:

$$P_{K\text{-}L3} = \tau_K \cdot f_{K\text{-}L3} \cdot \omega_{K\text{-}L3}$$

Obviously all these probabilities are specific to each element.

Radiating a sample with x-ray radiation will produce scattered and fluorescent radiation. The spectrum resulting from the fluorescent radiation will be seen as intensity peaks at certain energies/wavelengths. Each peak corresponds to a specific electron transition in a specific element. The intensity of these peaks corresponds to the probability of fluorescence as described above, elemental concentration, and the intensity spectrum of the applied radiation. This implies the possibility of using resulting fluorescent radiation for element concentration measurements. Sample thickness, geometrical configuration of instruments, and concentrations of other elements in the sample also influence fluorescent intensity.

Objectives

This thesis aims to increase the knowledge of x-ray based dendro analyses of wood to establish a base for future research on the effects of environment and silviculture on wood properties of typical boreal conifers such as Norway spruce (*Picea abies* (L.) Karst.) and Scots pine (*Pinus sylvestris* L.). The objective is to address the following questions:

(i) What is the performance of densitometric measurements using a batch scanning x-ray densitometer? That is, what are the effects of sample preparation, measurement parameters, and the relative size of different disturbances? Do drill cores need to be sawn to a constant thickness and what is the optimum thickness? Should resins be extracted from samples? What influence does fiber direction have? Are there differences between sapwood and heartwood? (Paper I).

(ii) What is the degree of measurability of different trace elements in wood samples from Scots pine and Norway spruce using energy dispersive x-ray fluorescence (EDXRF) analyzing technique? (Paper II).

(iii) Can changes in the environment be detected by EDXRF analysis on wood increment cores? Do element concentrations in tree rings from Norway spruce trees exposed to heavy metals-rich and acidified soil water from an old mining area differ in comparison to element concentrations in tree rings from trees grown in a reference area unaffected by the mine? Is there a decrease in influence from the mining area on the elemental concentrations in trees with increasing distance from the mine and with increasing distance from a stream with water from the leach reservoirs of the mines? (Paper III).

(iv) For which elements in Scots pine (*Pinus sylvestris* L.) is it possible to obtain estimates of element concentrations that are significantly different between adjacent tree rings and further separated tree rings? (Paper IV).

(v) For which elements and in which tree rings do additions of acid, lime and fertilizers influence tree ring element concentrations in Scots pine (*Pinus sylvestris* L.)? (Paper V).

Material and methods

To answer the questions of above, wood samples of Scots pine (*Pinus silvestris* L.) (I, II, IV, and V) and Norway spruce (*Picea abies* (L.) Karst.) trees (I, II, and III) were used. Samples were taken either as drill cores from standing trees (I, II, and III) or as disks from felled trees (II, IV, and V). In paper (I) young and old trees at Svartberget Experimental Forest in Vindeln were compared, in (II) sample trees of 45 to 125 years age and from different biotopes in different parts of Sweden were selected to get samples with a variation in element concentrations, in (III) spruce trees of relevant age in relation to the actual mining period were sampled from a mining area 40 km west of Skellefteå, and in (IV) and (V) samples were taken

from 50 years old pines in an fertilization experiment (Norrliden) 70 km NW of Umeå.

From the discs, 1x1-cm thick rods were extracted using a band saw. The samples were air-dried at room temperature to stabilize the moisture content of the samples to <15%. A part of the samples in (I) were submerged in a 9:1 mixture of acetone and water for 72 hours to remove extractives. Both drill-cores and rods from the discs were cut to a constant thickness using a mechanical twin or triple blade saw (Fig. 2). Drill cores in (I) were analyzed before and after cut to a constant thickness. For analyses of element concentrations, a plastic (PMMA) standard was prepared in the same way as the wood samples (II, III, IV, and V).

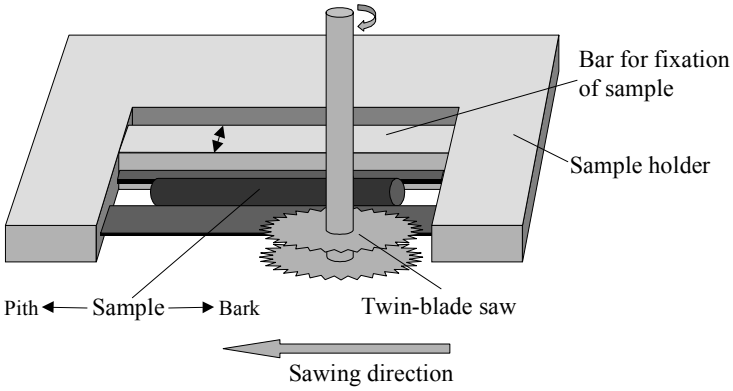

Fig. 2. Schematic of the sawing equipment.

Both microdensitometry and element concentration measurements were done using a Woodscanner built by Cox Analytical Systems AB (Fig. 3). The array sensor was used for density measurements and the EDXRF detector for the concentration measurements. Up to 20 samples could be analyzed in each batch measurement and the measurements are completely automated after mounting the samples in the Woodscanner and entering some measurement parameters in the beginning of the analysis. Three different types of x-ray tubes were used in analyses; Cr (II), Cu (I and II), and Mo (II, III, IV, and V). Voltage and current to the x-ray tubes were set between 35-60 kV and 30-55 mA. The elements measured were Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, Ga, Sr, and Ba. The calculations of densities and concentrations from the raw data produced by the Woodscanner were done using local software and software produced by Cox Analytical Systems AB.

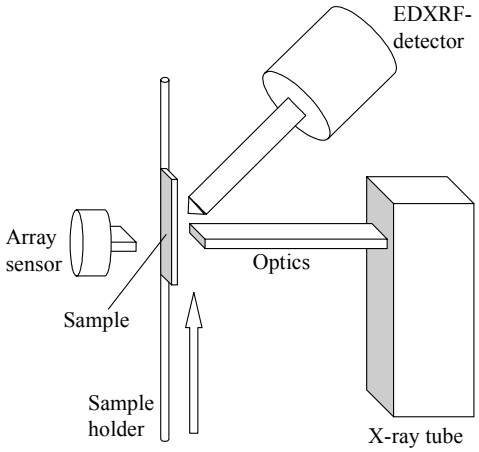

Fig. 3. Devices set-up in the Woodtrax.

In (I), (III), (IV), and (V) statistical analyses were performed using the general linear models (GLM ANOVA, nested models or simple factorial) procedure of SPSS (Norusis 2000). Tukey and Dunett T3 post-hoc tests were used in (I) and Bonferroni post-hoc test was used in (III). In (II) calculations of Poisson probabilities were done to evaluate statistical quality in measured element concentrations and regression analysis was used to evaluate accuracy in concentration measurements.

Microdensitometry of conifer wood

An important factor in microdensitometry is sample preparation. Softwoods commonly contain substantial amounts of resins and the resin content is unevenly distributed within the wood, such as between heartwood and sapwood. Resins are especially evident in Scots pine but may also be important for wood density measurements in Norway spruce (I). The resins cause increased wood density because resins marginally influence wood volume, but they can also effect x-ray attenuation and cause errors in wood density measurements (I). This is caused by differences in element composition between wood and resins, and means that resins should be extracted from wood before microdensitometric measurements are obtained (I).

As mentioned above, high resolution in microdensitometric measurements is needed to recognize tree rings and structures within the rings. It is possible to reach high technical resolution, below 0.05 mm, in direct scanning microdensitometry (Jonsson *et al.* 1990; I). Problems with resolution in microdensitometric measurements usually concern tree rings not being parallel to the x-ray beam penetrating the sample (Fig. 4). For this reason, it is advantageous to use thin samples. The samples should also be aligned with the tracheids extended in the direction of the x-ray beam to use as parallel and straight tree rings

as possible. Another reason to cut samples, besides the requirement to have thin samples, is to get a precise and well-defined thickness. It is possible to cut samples to a thickness of 1 mm and still have a mean standard deviation in thickness below 1% (Larsson *et al*. 1994). The alignment of thin samples with the tracheids parallel to the x-ray beam may cause errors in density measurements due to x-rays passing through the cell lumen (Moschler & Winistorfer 1990). This can be avoided either by slightly turning the sample or by using thicker samples. For Norway spruce and Scots pine, a turn of 2.4º should be enough for 1 mm thick samples (Larsson *et al*. 1994) and 5 mm thick samples differ less than 1% in mean density due to the way tracheids are aligned – parallel or perpendicular to the x-ray beam (I). It is also possible to use intact drill-cores directly and calculate thickness from sample width and shape. This results in less precision and increased mean deviation from calibration measurements in measured density from 1% for sawn samples with a thickness of 2-8 mm to 1.6% for 5 mm thick intact drill-cores (I). The thickness calculations for intact drill-cores also require adjusted software (I).

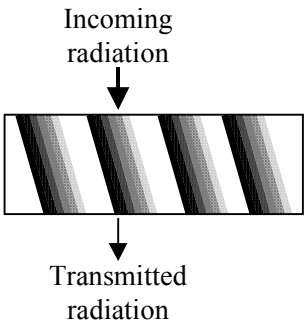

Fig. 4. Resolution disturbances from geometry of tree rings in microdensitometric measurements.

The optimal wavelength of x-ray radiation in microdensitometry is correlated to wood type, element composition and sample thickness (Olson *et al*. 1988). The optimal thickness of samples thus depends on element composition and the wavelength of the x-radiation. The optimal thickness for Norway spruce and Scots pine samples using a Cu x-ray tube at 40 kV is approximately 5 mm, but a decrease of the thickness to 2 mm did not significantly affect precision (I).

From the above descriptions of x-ray interactions with wood, it follows that each calculated attenuation coefficient is only valid for a specific element composition using one specific radiation energy. Thus, the radiation should be monochromatic. The attenuation can be calculated either theoretically, provided the element composition is known, or by using a standard with known density and the same element composition as the samples to be analyzed. The use of theoretically calculated attenuation is complicated by the need for calibration of the instrumental constant, because this is not constant over longer periods. By measuring the mean density of the samples volumetrically and gravimetrically, the samples can then be used as standards (I). If the variation in attenuation coefficient between the samples is small, then it may even be possible to use only a subset of

the samples as standards (I). To exclude the influence from moisture content in samples on measured densities calibrations should be done using oven dried samples. If the moisture content varies within the sample, then these errors will not be calibrated for and the errors will increase due to higher attenuation for water compared to wood. Water has approximately 1.3 times higher attenuation than wood for x-radiation of 6 keV (Larsson *et al*. 1994). This would mean that a deviation of 1% from mean moisture content in a sample produces an error in measured wood density of 1.3% (1 · 1.3). With an air temperature between 15° and 20°C and a relative humidity between 20% and 40%, the moisture content in wood samples will be between 4.5% and 8% at equilibrium (Larsson *et al*. 1994). To reduce errors from variations in moisture content within samples, the samples should be measured after being equilibrated to a stable and low relative humidity at room temperature.

Using conventional diffraction x-ray tubes in combination with a flat beam collimator produces pseudo-monochromatic radiation (Rindby *et al*. 1989). However, this radiation is not monochromatic enough to provide constant attenuation coefficients for individual samples with a varying mass-thickness (density multiplied by sample thickness) (I). To compensate for this, a special type of standard is needed, which has a constant attenuation coefficient – a homogenous density and element composition, but a varying mass-thickness. This standard makes it possible to produce a curve that describes the relationship between attenuation coefficients and mass-thickness. This standard should have an elemental composition similar to wood, since the shape of this curve is influenced by the element composition. The level of the curve should be calibrated using the sample mean density as described above.

In the early 1960s, H. Polge started to develop microdensitometry by exposing wood samples put on x-ray film with x-radiation (Polge 1978). In the 1980s, microdensitometric studies were simplified by the development of direct reading x-ray densitometry (Jozsa *et al*. 1987; Jonsson *et al*. 1990). Today, by careful sample preparation and calibration, densitometric measurements using a batch scanning x-ray densitometer offers rational density measurements with high resolution and high precision (I).

Analysis of tree ring element concentrations by EDXRF

In quantitative EDXRF measurements, the relationship between fluorescent intensity and elemental concentration is used as described above. This relationship is influenced by the content of other elements within the sample. The influence from other elements (matrix effects) can either enhance or suppress fluorescence from an element within a sample. In concentration calculations these effects can be treated in different ways, either calculated directly from fundamental physical properties or treated as coefficients describing the relationship between all elements (Lachance & Claisse 1995). The coefficients can be estimated either

theoretically or empirically. However, the problem is that to calculate the concentration of one element, the element content of all other elements needs to be known. This can be expressed as a compound equation that can be solved iteratively (Kuczumow 1996, II).

The use of polychromatic radiation in quantitative EDXRF measurements demands that the intensity spectrum from the x-ray source is known. For most commercial x-ray sources (x-ray tubes), this can be accomplished by the use of tabulated spectra (Jenkins 1999). Another solution is the use of scattered radiation from the sample to calculate the x-radiation intensity spectrum before the radiation penetrates the sample (II). This requires knowledge about the element composition of the sample, which first can be assumed and then calculated iteratively from calculated element concentrations. Both iterations, here and in the paragraph above, are facilitated by the fact that wood has a relatively stable chemical composition where mineral elements (ash content) contribute less than 1% of the mass (Fengel & Wegener 1984).

The calculations of concentration from measurements of fluorescent radiation can be divided into four steps: (i) instrumental calibration, (ii) calculation of incident intensity spectrum, (iii) density calculations, and (iv) element concentration calculations. For the instrumental calibration, a homogenous standard sample with known element composition and density, e.g., a PMMA stick, can be used (II). The element composition should be as similar as possible to the element composition of the analyzed wood samples. Calculations in step (ii) to (iv) are repeated iteratively where the element contents are estimated in the first iteration. Theoretically, these calculations should produce accurate concentrations. However, errors are produced in the different steps, e.g., from approximations such as the element composition of the samples in steps (ii) to (iv). In the future development of the methodology, these errors need to be reduced and calibration methods need to be developed (II).

In (II) it was concluded that the accuracy in EDXRF measurements could be improved by more precise sample mounting. According to this a new sample holder, for which the sample alignments could be adjusted, was built. The new sample holder resulted in much more even level of spectrum background (scattered radiation) in spectrum from different measurements and thereby in better accuracy in measured densities and concentrations. This also resulted in that the calculations of the incident intensity spectrum (step (ii) above) could be improved by using the spectra of the reference sample for background fitting. In this way the accuracy of measurements in (III), (IV), and (V) were considerably improved compared to measurements in (II).

Using measuring technique based on energy dispersive x-ray fluorescence makes it possible to measure several trace elements simultaneously (II). Elements that can be measured are Ca, Mn, Fe, and Sr and in most cases also K and Zn. Elements that also may be possible to measure with improved technique are Cl, Ni, Cu, Ga, and Ba. Two factors determine if an element is possible to measure – the sensitivity of the measuring technique and the element content in the sample. The variations in sensitivity between different elements are relatively small for

elements with atomic numbers higher than Ca (20) (II). This makes the element content crucial if an element is to be measured. With improved techniques for EDXRF analysis, additional elements may be possible to measure. Two elements with relatively high concentrations that might be possible to measure are Sn and Pb (Table 1), whereas Hg probably will not be measurable. The reason that K and Zn cannot always be measured is partly due to a high variation in content between samples from different trees (II). Fe and Sr have a smaller variation in content between samples, which probably explains why these elements are easier to measure. A high variation should be beneficial because it is easier to detect differences in element content between samples and a high variation may indicate a higher degree of influence from the environment on the element content in wood. The large differences in concentration between different measurements of elements in Table 1 should not be taken as proof of a high variation, because some of these differences might be due to systematic differences in the measurements.

Table 1. *Data on typical concentrations of different elements in stem wood from pine (Pinus sylvestris L.) and spruce (Picea abies (L.) Karst.) in mg kg^{-1} (ppm) dry weight. Numbers within brackets indicate number of observations*

Elements	Harju *et al.* (1997)		Nilsson (2000)		Häsänen & Huttunen (1989)
	Spruce (5)	Pine (4)	Spruce (7)	Pine (2)	Spruce (5)
Mg			95.1	119.6	131
Al			2.20	5.40	4.2
Si			4.38	1.002	
P	47	68	9.187	11.57	38
S	79	103	896	911	56
K	743	548	334.2	269.0	390
Ca	1153	739	687	499	930
Mn	36	44	96.0	75.7	65
Fe	2.6	3.2	6.151	10.59	
Ni	0.15	0.18	0.161	0.0814	
Cu	0.74	1.13	1.258	0.858	
Zn	6.36	5.24	11.576	9.778	8.4
Rb	0.82	0.58	1.159	1.902	2.2
Sr	8.28	3.06	3.967	3.426	
Ag		0.12			
Cd		0.27	0.090	0.213	
Sn		0.48	12.11	2.486	
Sb			0.504	0.0894	
Ba	11.4	0.7	8.85	5.50	
Hg			0.00354	0.00356	
Pb	0.28	0.19	27.8	5.23	

Possibilities using x-ray based dendroanalysis

The relationship between silviculture/environment and wood properties is usually complicated and involves unexplained variations. Therefore, it is important to be able to do large samplings in a cost-efficient manner. Because it is possible to do both microdensitometry and EDXRF analyses using radial increment cores, the sampling can be done in a non-destructive and cost-efficient way. This combination of rational non-destructive sampling and automated cost-efficient analyses provides opportunities for future research and a more property adapted use of wood raw material.

A possible future area of application for microdensitometry and EDXRF analyses is the characterization of the raw material from the forest to the industry. At first, this can be done using sampling tests, but as knowledge increases, the tests can be supplemented and/or exchanged with prediction models. The prediction models will be able to predict properties from data derived from soil conditions, element depositions, silviculture, climate, age etc. Important properties in construction timber, for example, are elasticity and strength and in pulp and paper making, fiber properties are essential. Most of these properties cannot be measured directly by microdensitometry, but it can still be useful. Elasticity and strength (Hudson 1967; Siimes 1967) and fiber properties (Madhu *et al*. 1992) are directly correlated to density. There are also indirect correlations in other properties, such as the presence of juvenile wood, latewood, and reaction wood, which in turn can be evaluated by microdensitometry (Edlin 1965; Steffen *et al*. 1997). The element content can in some cases also be an important wood property for manufacturers, such as in the industrial bleaching processes of pulp (Ulmgren 1997). In many cases the influence of trace elements can be assumed insignificant for wood properties because trace element content in wood is quite low (Table 1).

Tree rings, which usually are easily distinguished in boreal softwoods, strongly facilitate the usefulness of dendro analysis of density and other structures related to density as well as element content. The use of tree rings in dendro analysis offers information both on spatial distribution of these properties in wood as well as on temporal variations in the environmental factors that influence these properties. The development of x-ray based dendro analysis should not only be focused on the ring but also on the structures within the ring. The greatest variation in wood density is found within the annual ring and is mostly governed by the proportion of earlywood to latewood (Megraw 1985). As noted by Barbour *et al*. (1997), it should be possible to detect structures within the ring that are produced during the earlywood or latewood formation. Furthermore, the density in different parts of annual rings may correlate to environmental properties differently, e.g., for Norway spruce (Wimmer & Grabner 2000) found latewood density and maximum density having highest correlation with temperature and precipitation.

Trees recover trace elements mainly through their roots, but also from the atmosphere through their leaves and bark. Trees deposit some of these elements in the newly formed wood. This is the foundation of dendrochemical analysis where

measurements of trace elements in annual rings record historical changes in a tree's environment (Lewis 1995). It has been possible to use the content of trace elements in annual rings as indicators for the following:

- high environmental load of heavy metals (Hagemeyer & Markert 1993)
- changes in nutritive status within stands (Cote & Camire 1995)
- soil acidification, manganese as an indicative element (Tendel & Wolf 1988; Guyette *et al*. 1992; DeWalle *et al*. 1995)
- climatic changes (McClenahen & Vimmerstedt 1993)
- general health of a tree (Lewis 1995)

Dendrochemical analyses provide possibilities for environmental supervision in a vast area of applications. Advantages of dendrochemical analyses are the common occurrences of trees in most environments, their relatively high spatial resolution, and the possibility to provide a temporal dimension where the annual rings display a historical environmental archive. There are both positive and negative experiences from applications of dendrochemical analysis. For example, the results from studies correlating heavy metal deposition rates and element contents in annual rings vary. There are examples that demonstrate correlation (Eklund 1995; Watmough & Hutchinson 1996), uncertain correlation (Zayed *et al*. 1992), and no correlation (Garbe Schoenberg *et al*. 1997) between heavy metal deposition and element contents in annual tree rings. In addition, studies that correlate fluctuations in soil chemistry with element content in annual rings present both supporting (Levy *et al*. 1996) and conflicting (De Visser 1992) results. A probable reason for these varied results is that the fundamental prerequisites for dendrochemical analysis have not always been fulfilled. These prerequisites, according to Hagemeyer & Markert (1993), could be expressed as follows:

(1) A distinct and constant relationship must exist between the element concentration in the environment and the amount incorporated in wood tissue.
(2) Incorporation of the investigated element into certain annual rings must occur only within a limited time.
(3) It should be known to which rings the element is transported, either only to the outermost and youngest rings or to a number of older rings.
(4) After incorporation of the element in an annual ring, no subsequent remobilization and re-translocation should occur.
(5) The radial distribution pattern of an element in the trunk wood should be stable over a long period (temporal stability).
(6) Radial distribution patterns of certain elements should be similar in different parts of the same tree (spatial stability).

All these prerequisites will probably not be completely fulfilled for any element within any tree species. It is crucial, though to investigate to which degree they are fulfilled to be able to evaluate the usefulness of dendrochemical analysis.

Regarding relations between the environment and the element concentration within wood, soil pH and Mn concentration within tree rings seems to be correlated. In study (II), Norway spruce and Scots pine trees grown on lime rich soils had lower concentrations of Mn compared to trees from more acidic sites. In

study (III), Norway spruce trees close to an acidified stream had higher Mn concentrations compared to trees further away from the stream and in study (V) Scots pine trees supplied with acid had higher and trees supplied with lime had lower tree ring concentrations of Mn then compared to trees without these supplications. This relation with a negative correlation between soil pH and concentration of Mn in wood of trees is also found in several other tree species (Guyette *et al*. 1992). Potassium has a relationship between element concentration in wood and the environment that is more difficult to interpret. Decreased concentrations of K were found in wood from both Norway spruce and Scots pine trees growing close to an ore smelter (II). Elevated K concentrations have also been found in spruce trees within an old mining area. In trees closest to a stream with contaminated water from the mine, though, the K concentrations were not elevated (III). When Scots pine trees were supplied with acid or lime no effect on the K concentration within tree rings could be observed (V). One interpretation of this could be that heavy metal contamination reduces uptake of K by the trees and that this gives lower concentrations of K in trees exposed to heavy metals, but this does not explain the increased concentrations of K in trees within the mining area in the study (III). The concentration of K within tree rings is probably related to the availability of K in the soil as indicated by the increase in K concentration in fertilized (NPK fertilization) Scots pine trees (V). The only sign of a relation between contamination of heavy metals and concentrations of heavy metals in tree rings were for Zn. For trees close to an ore smelter, elevated concentrations of Zn were found in trees of Norway spruce but not in Scots pine (II). There were indications of elevated Zn concentration in Norway spruce tree close to a stream with contaminated water from an old mine (III). It is also shown by Hagemeyer & Lohrie (1995) that elevated Zn concentrations in the soil can increase the concentration of Zn in tree rings of Norway spruce plants.

Regarding prerequisites 2 and 3 above – time interval elements incorporated into a specific tree ring and to which tree rings elements are transported – it is indicated both for K and Mn that these elements are incorporated into each tree ring of Scots pines for several years (V). For Norway spruce it has been demonstrated that both Zn and Cd are transported to several tree rings when supplied to plants (Hagemeyer & Lohrie 1995). This means that dendrochemical analysis cannot be used with a resolution of single years for these elements. After heartwood formation, no transportation of elements to the tree rings should occur, since there is no xylem sap transport and no active cell transport within heartwood. This means that the resolution of dendrochemical analyses should not exceed the number of tree rings within the sapwood.

Prerequisites 4 states that elements should not be remobilized. The occurrence of remobilization is found in tulip trees (*Liriodendron tulipifera* L.) for P, K, and Zn (McClenahen *et al*. 1989). The occurrence of remobilization of elements should mean that differences in concentrations between adjacent tree rings should disappear and then prerequisite 5 could not be fulfilled. In (IV) it was proved that significant differences in element concentration between adjacent tree rings could be found for K, Ca, Mn, and Zn within Scots pine trees. For black spruce (*Picea mariana* (Mill.) BSP) the radial distribution patterns for K, Ca, Cr, Mn, and Fe are

detectable for at least a century (Martin *et al*. 1998). This indicates that prerequisite 5 should be fulfilled and that prerequisite 4 should be at least partially fulfilled, meaning that some part of the elemental content within a tree ring can not be remobilized.

In (IV) the radial distribution pattern of K, Ca, and Mn between adjacent tree rings were found to be significantly different in different geographical directions within stems of Scots pine. This means that prerequisite 6 is not fulfilled. The differences were relatively small, though, and significant differences between adjacent tree rings could still be detected for all three elements.

Conclusions

For microdensitometry measurements, it was possible to use intact drill-cores directly, but sawing the samples to a constant thickness increased precision from 1.6% to 1% in mean deviation from calibration measurements. The use of thin samples aligned with the tracheids in the direction of the x-ray beam provides the highest resolution of annual rings. However, this is linked with the risk for errors in the density measurements due to x-rays passing through the cell lumen. Thickness and alignment should be adapted to give optimal resolution without loss of precision. Samples should be extracted to remove resins before wood density measurements

The use of quantitative EDXRF technique for measurements of trace elements in tree rings is limited to which elements that can be measured. Elements that can be measured are Ca, Mn, Fe, and Sr. In most cases can also K and Zn be measured. EDXRF needs though to be calibrated to acquire accurate concentrations. Elements that also may be possible to measure with improved techniques are Cl, Ni, Cu, Ga, and Ba. The use of x-rays for batch analyses of density and trace elements in tree rings offers rational and cost-efficient analyses.

Differences in tree ring concentrations due to variations in the environment of Norway spruces could be found for six elements (K, Ca, Mn, Fe, Ni, and Cu). Investigating the influence from mining activities on the tree ring concentrations, the only relation that could be found was between Mn tree ring concentration and acidification from the mine. It is concluded that EDXRF analysis could be suitable for tracing environmental changes that affect elemental content in Norway spruce wood although higher sample numbers than those used in the present study are needed to improve the measurement accuracy and the cover of geographical differences.

Significant differences in concentrations between tree rings in Scots pine indicate that dendrochemical analyses can be used for K, Ca, Mn, Fe, and Zn. For Mn, it seems possible to use tree ring concentration as an indicator for soil acidity. It may also be possible to use tree ring concentrations of K as an indicator of available K in the soil.

Future research

The use of quantitative EDXRF for dendrochemical analyses requires some kind of verification of the accuracy in measurements. Calibrations can be done by parallel measurements using a calibrated measurement method or by the use of standards with known element concentrations. The use of a parallel measurement method should probably be preferred as standards always will have a slightly different matrix compared to measured samples and the differences in matrix effects between samples and standard will be difficult to estimate. The problem using a calibrated measurement method is that it must allow analyses of very small samples, e.g. single tree rings from drill-cores. A solution to this could be to use total reflection EDXRF on dissolved samples. To use the available analyzing equipment for total reflection EDXRF a new sample holder and appropriate methods for dissolving small wood samples need to be developed.

For most elements in tree rings of Scots pine and Norway spruce, it seems that the concentrations are due to environmental conditions during both the year the tree ring was developed and several years afterwards. How many years a tree ring is influenced by the environment and how this influence is distributed between different years for different elements in the two tree species need to be further investigated.

For K a relationship between K availability in the soil and K concentration in tree rings is indicated but more research is needed to clarify this relation. Other relations that also should be clarified are between soil contamination with heavy metals and tree ring concentration of heavy metals. In this case especially Zn but maybe also Ni and Cu should be interesting to investigate. Each relation between a specific environmental factor and the tree ring concentration of a specific element – e.g. soil pH and Mn tree ring concentration – need to be thoroughly investigated before it can be used for dendrochemical analyses. This includes how the relation is influenced by different environmental and tree physiological factors such as soil chemical properties, tree age, climate etc.

Microdensitometry and EDXRF analyses could be used in the direct characterization of the raw material from the forest to the industry. However, a more efficient way for characterization would though be to develop models to predict density and element content from data derived from soil conditions, element depositions, silviculture, climate, age etc. Wood density and element concentration are in many cases related to other wood properties such as elasticity, strength, fiber properties, and reaction wood. By gaining more knowledge about these relations microdensitometry and EDXRF analyses could be used as cost efficient methods for estimations of other properties in trees.

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