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VARIATIONS OF ELEMENT CONCENTRATIONS IN TREE RINGS OF SCOTS PINE (*Pinus sylvestris* L.) IN THE VICINITY OF AN OIL SHALE-FIRED POWER PLANT

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Temporal distributions of chemical elements in the growth rings of Scots pine and underlying relationships among xylem element concentrations and anthropogenic air pollution exposures on a territory influenced by an oil shale-fired power plant were studied. The study site is located at Narva-Jõesuu, approximately 11 km northwest from the oil shale fired Baltic Power Plant. Alkalization of the soils caused by intensive industrial alkaline pollution has been detected. No relationships between the radial growth of trees and oil shale fly ash emissions of directly preceding years were detected. Significant positive relationships between radial growth and oil shale fly ash were detected if emissions older than 5 years were compared with the present growth. Concentrations of P, K, Zn, Cu, and Pb exhibited increasing general trends while the time trends for Ca, Mn, and Mg were decreasing. Considerable horizontal variation in the concentrations of Cr and Ni occurs but no general trend was observed. The results obtained for P, K, Zn, Cu, and Cr suggest strong relationships between the time trends in the concentrations of these elements and the amount of air pollutants deposited on the stand.

Introduction

Several methods can be used for studying various changes in the environment of tree growth. During the last decades concentrations of elements in xylem wood have been used to investigate changing air quality, including pollutant and metal deposition histories at forest sites [1–6]. In early studies, concentrations of elements in tree rings were used as indicators for delineating the timing and geographic extent of the impact of point pollution sources [7–9]. Other studies have used changes in elemental concentrations of xylem to detect air pollution trends, connected with dispersed pollutant sources such as Pb and other trace metal emissions from vehicles near highways and in urban areas [10–12]. Recently, concentrations of various elements in tree rings have been used to explain soil chemical changes in response to atmospheric pollutant deposition [13–16].

Dendrochemical detection of changes in the chemical environment of trees is based on concomitant changes in tree-ring elemental concentrations and relative immobility of the indicator elements in xylem. The potential lateral mobility and redistribution of elements within the stemwood complicates the interpretation of dendrochemical data. Chemical changes, associated with conversion of sapwood to heartwood and the association of some elements (e.g. P and K) with active metabolism in living cells, especially near the cambium, are likely the most important causes of these features. No common point of view exists in the literature on the potential mobility of particular elements in xylem wood, probably due to differences among tree species and xylem properties. According to earlier reports, lateral movement of Pb for tulip-tree (*Liriodendron tulipifera* L.) and hickory (*Carya* ssp.) [10], of Zn and Cd for Scots pine (*Pinus sylvestris* L.) [8], of Pb, Zn, and Cu for a number of tree species [7], and of P, K, Ca, and possibly of Pb for tulip-tree [17] has been detected. On the other hand, lateral mobility of Pb was not confirmed for white oak (*Quercus alba* L.) [10], of Cu and Pb for Scots pine [8] and of Al, Si, Fe, and Cu for tulip-tree [17].

Despite the lateral mobility of certain elements, correspondence among concentration profiles of various elements in xylem and changing elemental composition in the environment of tree growth has been shown. Pernestål and co-workers [18] investigated the changes in the elemental composition of Norway spruce (*Picea abies* (L.) Karst.) xylem after liming and acidification experiments and found an increased calcium, magnesium, and potassium content in the sapwood in the sample from the limed area, and high responses of Mn, Fe, and Cr in the sapwood to acidification. Increased concentrations of Ca in the sapwood of Scots pine after calcification were detected by Hantemirov [19] as well. He observed that more Cu is accumulated in the tree rings in the vicinity of a copper smelter formed during the years the smelter was functioning. Baes and McLaughlin [1] found increases in xylem accumulation rates of Fe and other trace metals in tree rings formed during the period when regional fossil fuel combustion emissions increased about 200 percent. Increased Pb in rings of trees near major traffic routes related to parallel increases in traffic density has been shown [20, 21]. McClenahen and co-workers [17] suggest that concentrations of Al, Si, Fe, Cu, S, and Sr in tulip-tree xylem could be useful biomonitors of soil chemical changes by virtue of their apparent immobility. The fact that sulfur has been reported to reflect air pollution patterns [3, 15] makes this element a good candidate as an indicator of air pollution. However, the results of the study carried out by Kadar [5] did not verify this indicator potential. She also noticed that concentrations of P, Sr, Ba, Ca, and Mg in tulip-tree xylem do not have strong connections to air pollution exposures.

The selection of tree species which minimizes radial redistribution of elements is important in dendrochemical research. The tree species selected for dendrochemical study should be long-lived, grow on a wide range of sites over a large geographic distribution, have a distinct heartwood with a low number of rings in sapwood, and have a low radial permeability [22]. Due to the more primitive nature of wood with tracheids and few short ray cells which reduce radial movement of the chemical elements in tree stem, conifers have a greater potential than deciduous species for constructing pollution histories from wood [10]. The most important conifers in Estonia, Scots pine and Norway spruce, are highly susceptible to air pollutants. These species, especially Scots pine, have been often used as indicator species by investigation of air pollution impact on forest ecosystems [6, 8, 23, 24].

Combustion of fossil fuels for electric power generation results in the release of chemicals that are likely to affect the surrounding soils and vegetation. Arp and Manasc [25] reported a loss of exchangeable Mg in soil and in red spruce (*Picea rubens* Sarg.) xylem coinciding with increasing proximity to the power generator. Long and Davis [2] detected regression relationships between elemental concentration of Sr in white oak and the distance from a power plant.

The primary objective of the present research was to determine temporal distributions of chemical elements in the growth rings of Scots pine, and to identify underlying relationships among xylem elemental concentrations and anthropogenic air pollution exposures.

Study Area and Methods

This research was carried out in the northeastern industrial region of Estonia. The topography of the study area is characterized by old postglacial sea dunes. The soils are well-aerated forest podzols. Dominant forest formations in the study area are dry boreal pine stands of varying age.

The study site is located at Narva-Jõesuu, approximately 1 km south of the Gulf of Finland and 11 km northwest from the oil shale-fired Baltic Power Plant, the main source of atmospheric pollution in this area. The power plant started operation in 1959. Emissions reached their maximum in 1990, showing a decreasing trend afterwards [26]. Pollutants emitted from the plant consist of hazardous gaseous components (SO_2, NO_x) and oil shale fly ash, which contains different phytotoxic elements [27, 28].

The stand at the study site is a multi-aged *Vaccinium*-type pine stand in which the dominant pines in the canopy are of age 160–200 years.

At the study site a dominant tree was sampled for chemical analysis, whereby lack of damage or defect was considered in sample tree selection. The sample tree for chemical analysis and three additional trees of the same age were cored from the northern and southern sides at 1.3 m above ground level with an increment borer for tree-ring studies. Then the sample tree was felled and a 10 cm disk was cut from the stem 1 m above ground. A soil pit was dug to a depth of approximately 100 cm within the crown area of the sample tree to describe and sample the O, A, E, B, and C soil horizons.

In laboratory each core, when dry, was mounted onto a grooved holder and the surface of the cores was cleaned using sandpaper. Then the cores were crossdated with each other, i.e. each tree-ring was assigned a calendar year, and the widths of tree-rings on cores were measured with a binocular microscope with a precision of measurement of 0.05 mm.

The wood disk was air-dried and the surface was cleaned with sandpaper in order to make the tree-rings more visible. Following the example of the crossdated cores the tree-rings on the disk were crossdated and the boundaries of each 5-year group of tree-rings (1990–1986, 1985–1981 etc. back to 1825–1821) were marked.

The xylem samples for chemical analyses were taken from the cleaned and marked side of the disk. For this purpose the wood surface was cleaned by drilling a 2-3 mm deep hole with a 5/16″ titanium twist bit in a drill. The generated shavings were dusted off the surface and discarded. The samples for chemical analysis were then taken with a 1/4″ cobalt twist bit from different holes until a sample weight of at least 5 g for each 5-year tree-ring group was obtained.

Elemental analyses on xylem were performed with a Shimadzu atomic absorption/flame emission spectrophotometer model AA-670. The concentrations of P, Ca, K, Mg, Mn, Cu, Zn, Pb, Ni, and Cr were measured. The sample from each soil horizon was analyzed for pH (0.1N KCl extraction), N(NO_3–N) (v/v soil/water), Mg and P (1N HCl extraction, colorimetry), and K and Ca (1N HCl extraction, flame photometry).

Emission data for the Baltic Power Plant for the period from 1959 to 1994 were provided by the State Enterprise *Eesti Energia*.

Descriptive statistics were computed for the chronology of each elemental concentration. Correlation and autocorrelation analyses using the programs STATGRAPHICS 5.0 and EXCEL 5.0 were carried out in order to describe the relations between the oil shale fly ash emissions and xylem elemental concentrations as well as to examine the radial growth of the trees in terms of the emissions. To remove the age-related biological growth trend of trees dimensionless tree-ring indices were computed. This was achieved by smoothing the time series of tree-ring widths fitting a negative exponential curve and dividing each measured ring width by the curve estimates.

Results and Discussion

Properties of Soil

The soil beneath the crown of the sample tree is a typical Podzol on sandy sediments with a weakly developed A-horizon. Occasionally these soils are acidic and base unsaturated [29]. Elemental concentrations in soil horizons and soil parameters are presented in the Table.

Chemical analysis revealed a strong impact of industrial pollution on the investigated soil. The concentrations of Ca, Mg, K, Zn, and Pb, which

Soil Parameters and Elemental Concentrations in the Soil Horizons Sampled beneath the Crown of the Model Tree

Horizons	Horizon thickness, cm	pH_{KCl}	Concentrations of elements, mg/kg									
			P	K	Ca	Mg	Mn	Zn	Cu	Pb	Cr	Ni
O	8.5	6.2	15	320	1150	110	977	112	3.9	35	11.4	8.9
A	2	6.3	21	164	700	64	797	79	2.8	31	10.8	6.8
E	7.5	4.4	4	5	25	3	2.4	2.7	0.5	0.4	0.7	0.1
B	12	4.3	27	5	25	11	1.6	0.7	0.4	0.1	1.5	0.1
C		4.7	151	2	50	3	7.1	0.6	0.4	0.5	2.1	0.1

dominate in the composition of oil shale fly ash, significantly exceed the dominant values of these elements in the humus horizon of Podzols in Estonia [30]. The pH value of the organic horizons of the Podzols in unpolluted regions is normally lower than the pH in the mineral soil horizons [31]. The high concentrations of Ca, Mg, and K in the organic horizons of the soil are apparently the most important contributors to the greater value of pH of these horizons compared to the deeper mineral horizons at the studied site. Such a pH anomaly is considered a criterion of alkalization of soils caused by intensive industrial alkaline pollution [32]. Alkalization of soils in North-East Estonia has been described also earlier [33, 34].

Significantly higher amounts of all microelements except Cu and Zn in the particulate matter deposited to the earth were reported at the observation station in Narva-Jõesuu as compared with data for most other observation stations [35]. In the present case, lower concentrations of Cu, Cr, and Ni and higher concentrations of Mn, Pb, and Zn than elsewhere in the humus horizon of the soils of North-East Estonia were detected. The lower than average concentrations of the soluble forms of microelements may be due to the composition of the parent deposits [35]. The most common reason of the Cu deficit in alkaline soils is the leaching of this element as a consequence of

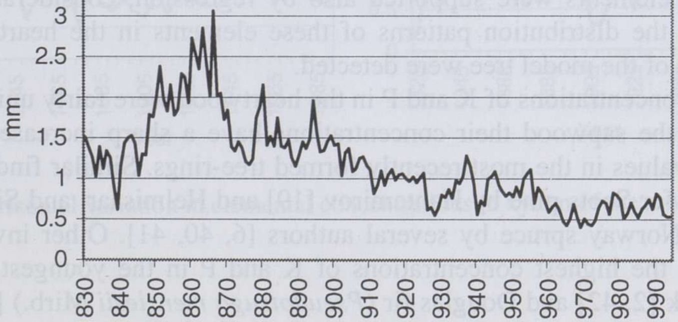

Fig. 1. Average tree-ring widths of trees from Scots pines stand at the study area

an elevated content of carbonates in soils [36, 37]. The higher concentrations of Mn, Pb, and Zn in investigated soil are apparently caused by the industrial dust emissions in this region.

Radial Growth of Trees

A long series of narrow tree-rings over the period from 1790 to 1840, visible on the cores, suggests that the sampled trees were growing in a closed-canopy stand when young (Fig. 1). The accelerated radial growth since about 1840 was apparently caused by thinning of the canopy. Maximum radial growth occurred in the middle of the 1860s at the age of trees about 85 years. The following renewed within-stand competition and the increasing age of trees led to a decrease in the radial growth. Against the background of the general decrease in the radial growth, a sharp increment drop during ten years following the maximum radial growth, and depression periods from 1926 to 1933 and from 1959 to 1975 may be distinguished. On the plot of ring widths, a tendency of increasing radial growth from about 1980 onward can be seen. The transition between heartwood and sapwood occurred around 1917.

No correlations between the elemental concentrations in the xylem and the radial growth of the model tree were found. Correlation analysis did not indicate the presence of relationships between the radial growth of trees and the oil shale fly ash emissions of directly preceding years. However, when emissions older than five years were compared with the present growth positive relationships were observed.

Distribution of Chemical Elements in Wood

The concentration levels of Ca, K, Mg, Mn, Cu, Zn, Pb, Ni, and Cr detected in the sample tree xylem were similar to those reported elsewhere for the stemwood of Scots pine [19, 38, 39]. Concentration patterns of these elements across the bole of the model tree are plotted in Fig. 2.

The graphs in the figure indicate that the concentrations of K, P, and Zn are increasing with time. Although general increasing trends in concentration of these elements were supported also by regression, considerable differences in the distribution patterns of these elements in the heartwood and sapwood of the model tree were detected.

The concentrations of K and P in the heartwood were fairly uniform over time. In the sapwood their concentrations have a sharp increase, with the highest values in the most recently formed tree-rings. Similar findings were reported for Scots pine by Hantemirov [19] and Helmisaari and Siltala [38], and for Norway spruce by several authors [6, 40, 41]. Other investigators recorded the highest concentrations of K and P in the youngest xylem of white oak [2, 42] and Douglas fir (*Pseudotsuga menziesii* Mirb.) [43]. Such increases in K and P concentrations are undoubtedly related to active metabolism connected with the physiological process of wood formation [44].

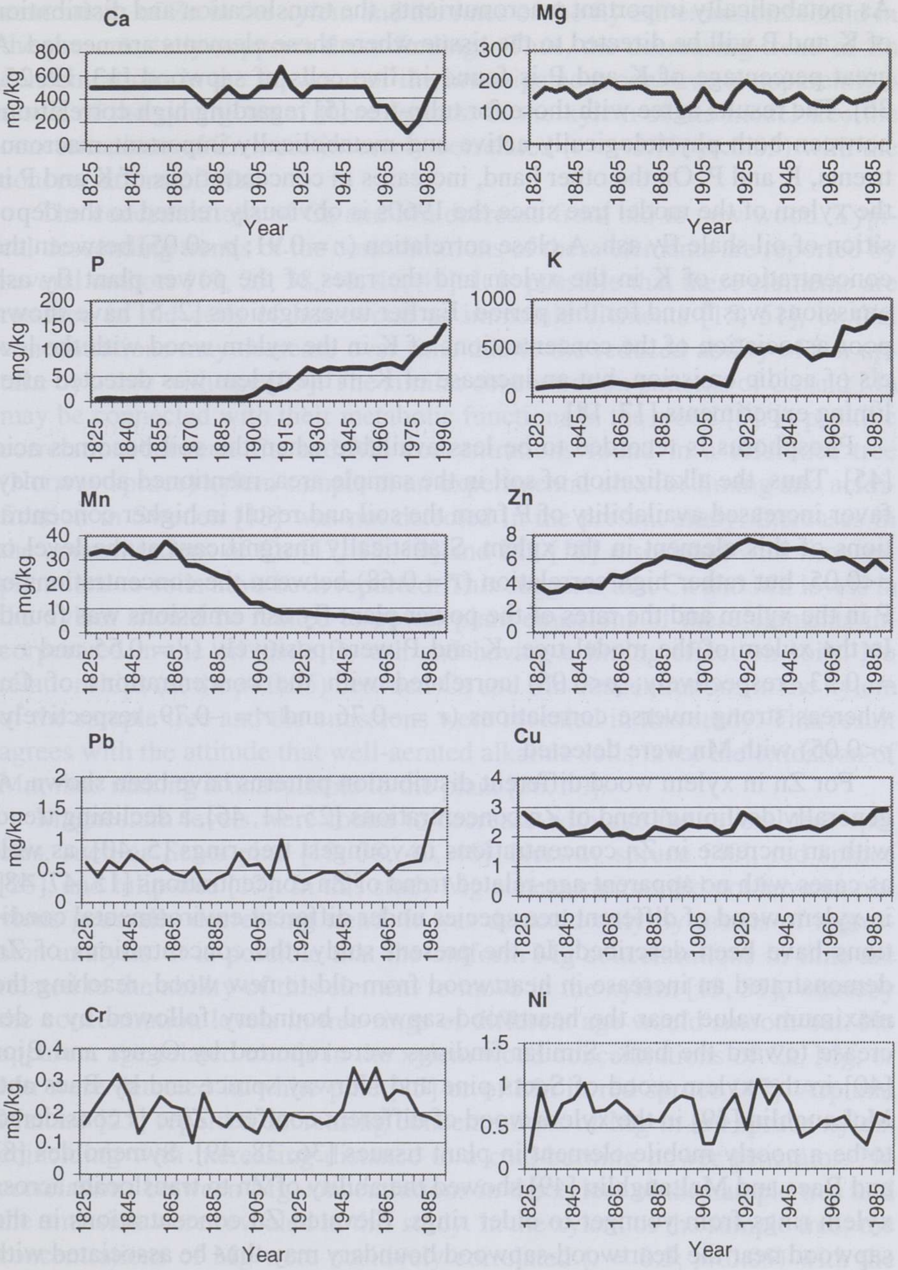

Fig. 2. Horizontal variation in elemental concentrations in xylem of the model tree

As metabolically important macronutrients, the translocation and distribution of K and P will be directed to the tissue where these elements are needed. A great percentage of K and P is found in live cells of sapwood [13, 19, 25, 36]. The results agree with those for tulip-tree [5] regarding high correlations between both physiologically active and metabolically important macronutrients, K and P. On the other hand, increases in concentrations of K and P in the xylem of the model tree since the 1960s is obviously related to the deposition of oil shale fly ash. A close correlation ($r = 0.91$; $p < 0.05$) between the concentrations of K in the xylem and the rates of the power plant fly ash emissions was found for this period. Earlier investigations [2, 5] have shown poor association of the concentrations of K in the xylem wood with the levels of acidic emission, but an increase of K in the xylem was detected after liming experiments [17, 18].

Phosphorus is recorded to be less available when the soil becomes acid [45]. Thus, the alkalization of soil in the sample area, mentioned above, may favor increased availability of P from the soil and result in higher concentrations of this element in the xylem. Statistically insignificant at the level of $p<0.05$, but rather high correlation ($r = 0.68$) between the concentrations of P in the xylem and the rates of the power plant fly ash emissions was found. In the xylem of the model tree, K and P were positively ($r = 0.55$ and $r = 0.53$, respectively; $p<0.05$) correlated with the concentrations of Cu, whereas strong inverse correlations ($r = -0.76$ and $r = -0.79$, respectively; $p<0.05$) with Mn were detected.

For Zn in xylem wood different distribution patterns have been shown. A generally declining trend of Zn concentrations [25, 41, 46], a declining trend with an increase in Zn concentrations in youngest tree-rings [5, 40], as well as cases with no apparent age-related trend of Zn concentrations [15, 47, 48] in xylem wood of different tree species under different environmental conditions have been described. In the present study, the concentrations of Zn demonstrated an increase in heartwood from old to new wood, reaching the maximum value near the heartwood-sapwood boundary followed by a decrease toward the bark. Similar findings were reported by Ogner and Bjor [40] in the xylem wood of Scots pine and Norway spruce and by Baes and McLaughlin [49] in the xylem wood of different conifers. Zinc is considered to be a poorly mobile element in plant tissues [36, 38, 49]. Symenoides [8] and Baes and McLaughlin [49] showed the ability of Zn to translocate across xylem rings from younger to older rings. Elevated Zn concentrations in the sapwood near the heartwood-sapwood boundary may thus be associated with the synthesis of heartwood substances in the transitional zone. Another factor influencing the Zn levels in the xylem wood is tree age. The data presented by Arp and Manasc [25] suggest that the availability of Zn in the soil may decrease with increasing stand age. The uptake of Zn from soil is greatly influenced by soil pH [49]. The availability of Zn decreases with increasing pH so that Zn deficiency may occur in plants growing in alkaline soils [36, 50]. The inverse correlation ($r = -0.83$, $p<0.05$) between the concentrations of Zn in the xylem and the rates of the fly ash emissions found in the present study supports these findings. Thus, the decreasing trend of Zn concentrations in the sapwood of the investigated model tree is apparently a result of the synergism of these factors. In the xylem of the model tree the concentrations of Zn were inversely correlated ($r = -0.79$; $p<0.05$) with the concentrations of Mn.

The concentrations of Ca and Mn decrease from old to new wood. Typical descending trends of the concentrations of these elements are reported by several authors [19, 25, 38, 40, 46, 49]. It is possible that these elements are retained in old cells of heartwood as immobile elements [15, 51], or that concentrations may decrease over time due to the reduced ability of ion uptake by a tree with age [25]. The similar concentration patterns of Ca and Mn may be connected with their metabolic functions in the wood [5]. A positive correlation between Ca and Mn concentrations found in a reference tree (Norway spruce) xylem sample at an experimental area for liming and acidification in Sweden [18] was not detected in the present study. Increases in the concentrations of Ca [17, 18, 19] and Mn [18] associated with lime applications to soils have been reported. This suggests that Ca and Mn levels in the xylem should be related to power plant emissions of these elements incorporated in the oil shale fly ash and having a liming effect on soils. No relationships (at the $p<0.05$) between Ca and Mn concentrations in the xylem of the sample tree and the emissions were revealed in this study. This result agrees with the attitude that well-aerated alkaline soils favor the oxidation of Mn, thus making it unavailable to the plant [36, 50].

Magnesium levels were found to decrease with age for several tree species, such as Scots pine [19, 38, 40, 46], Norway spruce [40], red spruce [25], and tulip-tree [17]. In this study Mg concentrations did not have an obvious generally decreasing trend. It was detected only by means of regression analysis. It is possible that the uniform Mg concentrations in time are related to the ability of this element to move in the xylem [19, 51], whereby the concentration levels in tree-rings of different age would smooth out. No apparent age-related trends in the xylem wood concentrations of Ca, Mg, or Mn were detected in white pine [15] or of Mn in red spruce [47]. Arp and Manasc [25] reported decreasing concentrations of Mg in red spruce xylem coinciding with increasing distance to a coal-burning power generator. No correlations between Mg concentrations in the xylem of the sample tree and the emission were revealed in this study. In the xylem of the sample tree, the concentrations of Mg were positively correlated ($r = 0.5$; $p<0.05$) with the concentrations of Mn.

The increasing trend of elemental concentrations in the most recently formed tree rings is evident for Ca and Mg, and less so for Mn. Similar findings were reported in a number of papers [1, 19, 25, 42, 48]. In several studies [1, 19, 39], the highest metal concentrations were found in living bark, phloem, and cambium tissues. The authors suggest that these elements can probably move from the phloem to the neighboring rings of the xylem.

Concentrations of heavy metals Cu, Cr, and Ni in the xylem have been found to increase and Pb to decrease from the center to the periphery of the stem by different authors [25, 40, 41, 47, 48]. In this study considerable horizontal variation in the concentrations of Cr and Ni was observed but no general trend was detected. The elements Cu and Pb exhibit irregular fluctuations, having flat concentration profiles in the heartwood, with increases in the sapwood. They reach a maximum in the most recently formed, nearest to the cambium tissue. Hantemirov [19], Baes and McLaughlin [49], and Arp and Manasc [25] have all reported similar results for Cu. Copper has not been found to translocate across xylem rings of Scots pine [8], but this was confirmed for a number of other species [7]. Baes and McLaughlin [49] report that the higher metal levels in more recent tissue may be related to increases in Cu deposition or reflect cycling transport from the phloem and the greater percentage of living cells in the youngest xylem. Correspondence between Cu concentration profiles and air-pollution histories have been shown by several authors [1, 8, 19]. High positive correlation ($r = 0.77$; $p<0.05$) between Cu concentrations in tree-rings and oil shale fly ash emissions found in this study suggests that the increasing concentrations of Cu with time since the 1960s may be related to Cu deposition in this area.

The availability of Pb declines in lime-rich soils [37]. By the same author, concentrations of Pb in the plant tissues depend largely on concentrations of this element in the soil. The concentration of Ca in the soil under the crown of the sample tree is high due to alkaline dust pollution (Table). On the other hand, high concentration of Pb in relation to the average status of this element in Estonian soils [35] is found in the same soil. Due to the low availability of Pb to the roots, especially in the case of the forest soils [37], there is a possibility that enhanced concentrations of Pb in the recently formed xylem of the sample tree may be due to direct absorption through needle tissues from the oil shale fly ash deposited on the needles, or to translocation from the phloem and cambial area where Pb concentrations are greater and cycling transport of this metal is occurring [39, 52, 53].

Arp and Manasc [25] reported that the increases in Ni and Cr in the recently formed wood of red spruce near a coal-burning power plant are related to increased availabilities of heavy metal ions in the forest stands and soils. Concentrations of Cr and Ni in the soil under the crown of the sample tree were lower if compared with the average contents of these elements in the humus layers of Estonian soils [30]. Kabata-Pendias and Pendias [37] suggest that the content of Cr in plant tissues may increase in conditions of elevated levels of anthropogenic emissions. In the present study, the concentration levels of Cr decreased in the xylem wood of the sample tree since the early 1960s. A strong negative correlation ($r = -0.85$; $p<0.05$) between the concentrations of Cr in the xylem wood and oil shale fly ash emissions during this period does not appear to verify these positions. Not much is known about the behavior of Ni in the stem wood. By some authors [54–56], the elemental concentrations of Ni in plants depend strongly on industrial air pollution. Kabata-Pendias and Pendias [37] reported lower concentrations of Ni in plants growing on soils with increasing pH values. The time trend for Ni reveals a number of unexplained elemental accumulation peaks in the present study, with relatively lower concentrations since the 1950s. No significant correlation between the concentrations of Ni in the xylem wood and oil shale fly ash emissions was detected. Neither Cr nor Ni were correlated with any element in the xylem wood.

The elemental distribution patterns in Fig. 2 show concentration peaks near the boundary between sapwood and heartwood for Zn, Ca, Mg, K, Cu, and Pb. Similar peak concentrations in the xylem of different tree species were reported by McClenahen and coworkers [17] for Fe, Cu, Zn, Mg, and K; by Wardell and Hart [42] for Mg, K, and Mn; and by Helmisaari and Siltala [38] for Mg and Ca. Such concentration changes in the transitional zone between sapwood and heartwood may arise from the intensified metabolism related to heartwood formation [6, 38, 42].

Conclusions

Alkalization of soils caused by intensive industrial alkaline pollution was detected. Correlation analysis did not indicate the presence of significant relationships between the radial growth of trees and oil shale fly ash emissions of directly preceding years. The presence of positive relationships between the radial growth and oil shale fly ash was detected when emissions older than five years were compared with the present growth.

Time trends of elemental concentrations were investigated for P, Ca, K, Mg, Mn, Cu, Zn, Pb, Ni, and Cr. The concentrations of P, K, Zn, Cu, and Pb exhibited increasing general trends, while the time trends for Ca, Mn, and Mg were decreasing. Considerable horizontal variation occurs in the concentrations of Cr and Ni but no significant general trend was detected. An increasing trend of elemental concentrations in the most recently formed tree-rings is evident for P, K, Ca, Mg, Cu, and Pb.

As metabolically important macronutrients, the translocation and distribution of K and P will be directed toward younger tissues where these elements are needed. Elements such as Ca, Mg, Cu, Pb, less Mn can move passively from the living bark, where the concentrations of these elements are high, to the neighboring rings of the xylem. Enhanced concentrations of Pb in recently formed xylem may be due to direct absorption through needle tissues from the oil shale fly ash deposited on the needles.

The results obtained for P, K, Zn, Cu, and Cr suggest strong relationships between the time trends in the concentrations of these elements and the amount of air pollution received by the stand.

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