

RADIAL PATTERNS OF 13 ELEMENTS IN THE TREE RINGS OF BEECH TREES FROM MAVROVO NATIONAL PARK, FYROM

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Abstract - The radial patterns of 13 elements (N, P, K, Ca, Mg, Fe, Na, Mn, Zn, Cu, Pb, Cd and Co) were analyzed in the tree rings of European beech (*Fagus sylvatica* L.). The study site was located in an "unpolluted" beech ecosystem in Mavrovo National Park. Thus, the obtained radial patterns in the beech trees were considered to be physiologically driven without significant pollution influence. The influence of the main climatic factors (temperature and rainfall) was tested. The radial patterns of individual trees were compared in order to find individual responses to environmental impacts. For most of the elements, higher concentrations were recorded in the pith and outer-most rings and lower in the middle part of the wood. The concentration of heavy metals was low, and followed the physiological patterns of other biogenic elements.

Keywords: Dendrochemistry, beech, radial patterns, elements, heavy metals, Macedonia.

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INTRODUCTION

Dendroanalysis or dendrochemistry was developed in, and has been used since the 1960s (Hagemeyer and Lohrie, 1995). It is a method of determining the mineral matters concentrations in tree rings. The concentration of elements in tree rings is used in the biomonitoring of the chemical parameters in the environment, including soil chemistry and atmospheric pollution (Meisch et al., 1986; Pennington et al., 1999). One of the most common assumptions is that the concentration of elements in tree rings corresponds to the availability of elements in the ecosystems in the period when tree rings were formed. However, the physiological processes can have an important role in the creation of the radial pattern of elements and thus mask the historical evidence.

Root uptake and vertical transport is the main pathway of nutrients in the stem. Uptake through bark and possibly foliage and subsequent incorporation into xylem should also be taken into account (Watmough and Hutchinson, 1996; de Vives et al., 2006).

The dendroanalytical method of biomonitoring can produce accurate pollution chronologies with a high time resolution only if the elements absorbed by the tree in a certain year are incorporated exclusively in the wood laid down in the same year. If a significant fraction of the absorbed elements is also transported into older annual growth rings, the time resolution of the resulting pollution chronology is reduced or completely lost (Hagemeyer and Lohrie, 1995; Nabais et al., 1999).

The practical evidence of the correlation of the radial patterns of some elements with atmospheric pollution (traffic pollution, industrial pollution, volcanic eruptions) has been confirmed in a number of studies (Meisch et al., 1986; Hagemeyer et al., 1992; Hagemeyer and Schäfer, 1995; Watmough and Hutchinson, 1996, 1999; Watmough et al., 1998; Watmough, 2002; Padilla and Anderson, 2002). However, there are cases in which the radial patterns of elements showed weak or no correlation with environmental impacts (Barnes et al., 1976; Hagemeyer and Schäfer, 1995; Nabais et al., 1996; Bindler et al., 2004; Watt et al., 2006).

Table 1. Soil chemical properties in the investigated beech ecosystem

Horizon	depth [cm]	humus	N	P	K	Ca	Mg	Fe	Na	Mn	Zn	Cu	Pb	Cd	Co
A0 f/h	5-10	10,28	1,541	0,038	1,50	0,030	0,38	1,56	0,034	0,060	104,2	12,75	9,46	1,35	7,69
A1	10-25	3,22	0,560	0,024	1,50	0,003	0,36	2,39	0,043	0,046	110,4	22,09	8,81	0,92	9,08
B	25-60	1,74	0,255	0,016	1,41	0,002	0,33	1,99	0,035	0,030	84,9	18,85	3,58	0,77	8,13
(B)C	60-80	0,97	0,207	0,015	1,39	0,002	0,35	2,39	0,041	0,025	83,4	19,88	3,90	0,78	8,03
C	80-120	0,81	0,197	0,017	1,22	0,002	0,31	2,24	0,041	0,028	95,5	21,90	6,61	0,96	7,89

According to Glass et al., (1993) the concentration of heavy metals deposited in tree rings depends on: 1) the rate of metal uptake from soil or atmosphere; 2) the transport mechanics of metals within the plant; and 3) the rate at which metals are deposited into xylem (= ring) tissue. The lateral exchange of heavy metals between bark and wood may also be an important factor in determining heavy metal levels in annual growth rings. It can be assumed that the concentrations of other elements in the tree rings depend on these mechanisms, as well.

It seems that the practical use of dendrochemistry depends on many factors. One of them is the characteristic of the tree species. The inability of some tree species to be used as temporal monitors of trace metal deposition may be due to the nature of the wood (Cutter and Guyette, 1993) which includes the potential of translocation in the wood. The value of dendrochemistry can be improved by the method proposed by Tommasini et al., (2000), who leached out the mobile fraction of Pb isotopes from the tree rings.

Watmough and Hutchinson (1998) found differences in the historical concentration of Pb in tree rings in an urban-rural gradient. In this study, Pb

concentrations in sugar maple tree-rings sampled from trees at a rural location, 150 km from Toronto, were consistently low.

Most of the other studies dealt only with the samples from polluted areas. The proper analysis of the dendrochemical data requires proper historical evidence of environmental factors as well as comparison with reference sites. In some studies, data on pollution trends were obtained and these were correlated with the element concentrations in the tree rings. However, the data on the climate parameters were often neglected and the physiological patterns were missing.

The radial patterns in beech trees from the research station in Mavrovo National Park can be used as reference since no pollution sources exist in the area. The influence of the temperature and rainfall was tested in order to reveal the physiological patterns of the radial distribution. In some of the dendrochemical studies it was documented that the trees from the same locality responded differently to the environmental impacts (Nabais et al., 1996). Thus, the radial patterns of beech trees were compared in order to find individual differences.

Study site

The presented work was conducted within the frames of the project "Complex ecosystem investigation in stationary conditions in the beech ecosystem *Calamintho grandiflorae-Fagetum* in Mavrovo National Park" (Grupče and Melovski, 1999). The station (20°48' E, 41 ° 42' N) is situated in well-developed middle aged beech forest on Bistra Mt., village Leunovo dystric, near Mavrovo Lake at an elevation of 1400 m. The community is developing on dystric cambisole soil type with a high humus content (Tab. 1). The climate is mountain-continental with Mediterranean influence (Filipovski et al., 1996).

Data according to Lazarevski (1993) based on the measurements of the meteorological station Mavrovo (1240 m), show that the average annual temperature is 7.1°C. The minimum average monthly temperature (below 0°C) is registered during the three winter months with a minimum of -2.2°C. The mean monthly maximum temperatures are measured in July (16.3°C) and August (16.0°C). The mean autumn temperature (8.2 °C) is higher than the spring one (5.8°C). The mean annual fluctuation of temperature is 18.7 °C.

The mean annual precipitation is 1103 mm. It consists mainly of snow and smaller amounts of rain in the warmer periods of year. From October to March there is over 100 mm precipitation per month, April and May are characterised by 80-100 mm, and July and August have less than 50 mm monthly precipitation. Permanent snow cover lasts 30-110 days while the snow period is 166 days in average.

Beech (*Fagus sylvatica*) absolutely dominates in the locality under investigation, with a density of 1200 trees ha⁻¹. The mean DBH of trees is about 16 cm. The shrub layer is represented mainly by beech and shrubs of fir (*Abies borisii-regis*). The herb layer has a low biomass (less than 6 kg·ha⁻¹). The most abundant herb species are *Anemone nemorosa*, *Dentaria bulbifera*, *Carex sp.*, *Brachipodium sylvaticum*, *Asperula odorata*, *Rubus sp.*, *Actaea spicata*, *Pteridium aquilinum* etc. Aboveground annual litter fall biomass is 4.98 t·ha⁻¹ while the average litter layer organic mass is 20.8 t·ha⁻¹.

MATERIALS AND METHODS

Twenty four beech trees for the determination of biomass were felled in the beech ecosystem (*Calamintho grandiflorae-Fagetum*) in October 1999. Discs from breast height of four trees (marked as trees #3, #14, #20 and #21) were cut and used for dendrochemical analysis. Samples were taken every five years (five tree rings), ground and used for chemical analysis.

In total, 13 elements were determined: N, P, K, Ca, Mg, Fe, Na, Mn, Zn, Cu, Pb, Cd and Co. Total nitrogen was determined by the semi-micro Kjeldahl method. The digestion of the samples was performed in a mixture of H₂SO₄, K₂SO₄ and Na₂S₂O₃.

Samples for the determination of phosphorus were digested in a mixture of HNO₃, H₂SO₄ и HClO₄. Phosphorus was determined by the method of Fiske and Subarow (1925). All of the metals (K, Ca, Mg, Fe, Mn, Zn, Cu, Pb, Cd and Co) were determined by atomic absorption spectrometry on a Varian AAS 10BQ.

The statistical analysis was performed in Statgraphics for Windows 2.0. The main type of analysis was second-order polynomial regression ($Y=a+bX+cX^2$).

RESULTS

Radial distribution patterns

The second-order polynomial model showed the best results in describing the radial pattern of all of the investigated elements. The results of the statistical analyses are presented in Tab. 1. In all of the cases the correlation coefficient (R²) was high.

The radial pattern of nitrogen, phosphorus and potassium showed highest concentration in the youngest rings and in the heartwood (Fig. 1). The mean concentrations of these three elements were 0.127, 0.0031 and 0.077 %, respectively (Tab. 2).

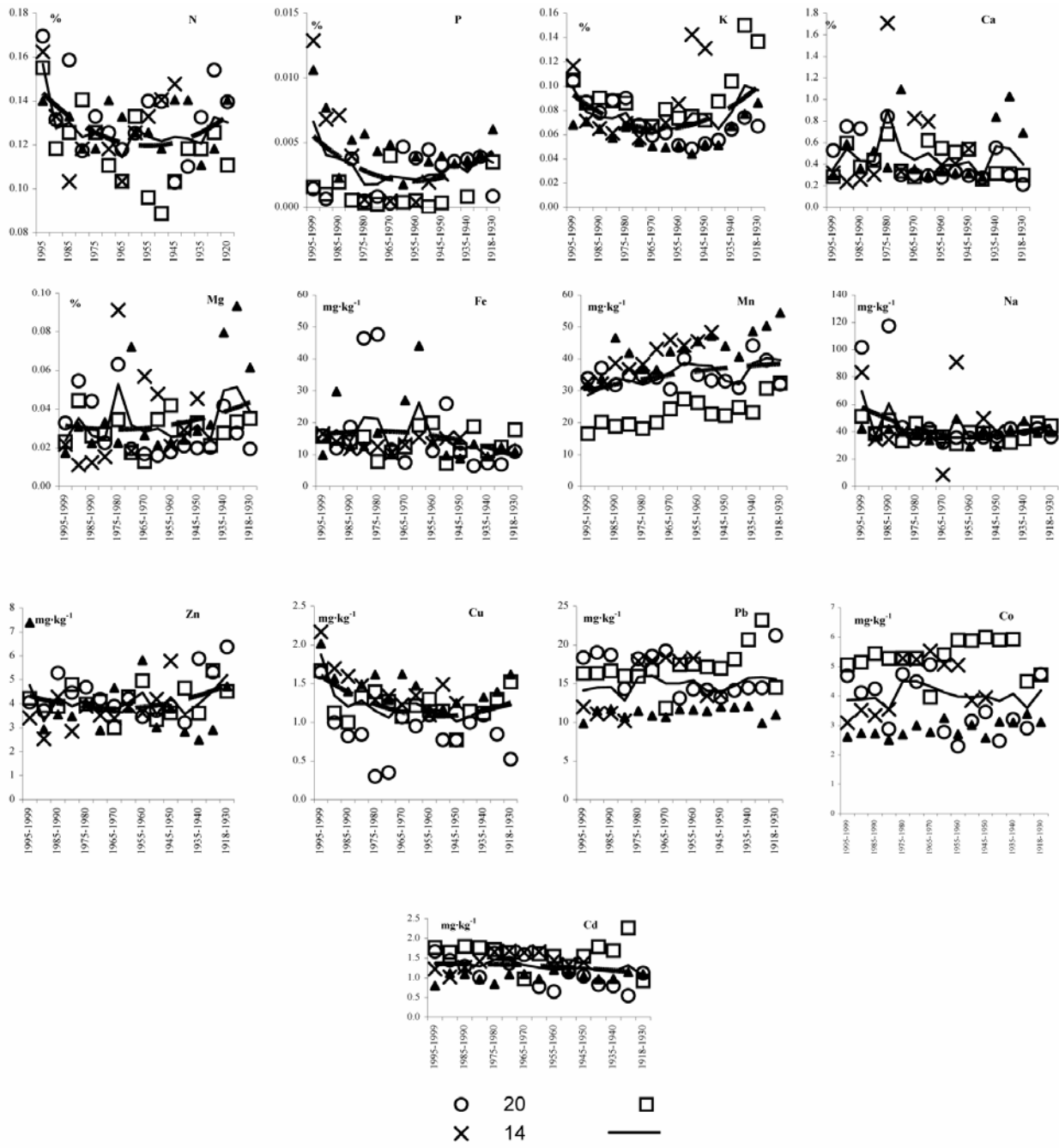


Fig. 1. Radial patterns of 13 elements in the tree rings of beech trees in Mavrovo National Park, Macedonia (numbers 20, 21, 3 and 14 correspond to the four analyzed trees).

Table 2. Minimum, maximum and average values of concentration in the wood of beech in beech forest in Mavrovo National Park.

	minimum	maximum	average
N	0.127	0.059	0.170
P	0.0004	0.013	0.0031
K	0.044	0.150	0.077
Ca	0.211	1.710	0.47
Mg	0.011	0.093	0.033
Fe	6.48	47.64	15.19
Mn	16.54	84.94	35.92
Na	8.72	117.41	42.57
Zn	2.50	7.39	4.09
Cu	0.30	2.17	1.22
Pb	9.83	23.19	14.88
Cd	0.55	1.27	1.28
Co	2.29	5.99	4.02

The group of sodium, zinc and copper had highest values in the youngest and oldest tree rings, similar to N, P and K.

Calcium showed an irregular pattern in the tree rings. It is interesting that both Ca and Mg showed an increase of concentration in the rings 1975-1980. The amplitudes of Ca concentration were significant. The minimal concentration was 0.211 and the maximum was 1,710 %.

Magnesium, manganese, iron and cadmium showed significantly lower values in the youngest and in the oldest tree rings.

Influence of climate (temperature and rainfall)

Tree ring concentrations of studied elements were correlated to the five-year averages of temperature and rainfall. The concentration of elements in the five-year-tree-ring groups was dependent on temperature in the case of N, P, K, Mg, Na and Cu. The amount of rainfall had significant influence only on Fe concentrations in tree rings. The rainfall amount had some influence on Cu concentration since the

multiple regression analysis (temperature and rainfall as independent variables) improved the correlation coefficient (Tab. 4). However, one should bear in mind that the set of analyzed values included the concentrations in the outermost rings that may distort the analysis in both directions: improving or decreasing the statistical indices.

The regression analysis of the response of individual trees to climate parameters showed a difference among the four model trees. Temperature was a dominant factor influencing the concentration of 10 elements in tree #20. Rainfall had a lower impact which was almost equally expressed in all four model trees.

Differences between individual trees

It is clear that the concentration of some elements was different in the investigated beech trees. Trees #20 and #3 had opposite concentrations of P, Mn, Pb, Cd and Co. The concentrations of Pb, Cd and Co were higher in tree #20, but the same tree had lower concentrations of P and Mn. Tree #3 had an opposite pattern: the concentrations of Pb, Cd and Co were lower, but this tree had higher concentrations of P and Mn.

Fisher's LSD test was used to determine differences and homogenous group (Tab. 6). Co concentration was significantly different in all four trees. Similar results were obtained for other heavy metals, Mn, Cu, Cd and Pb, where the homogeneity was recorded in 1-2 combinations at most. P and K concentrations were different in 3 out of 6 combinations. N concentrations were different only in the case of model trees 20 and 21. In the case of Ca, Mg, Fe, Na and Zn the analysis showed that all of the trees have similar concentration values i.e. there were no statistically significant differences among individual trees.

DISCUSSION

The radial pattern of N concentration showed highest values in the youngest and the most active tree rings. Such a pattern was recorded in other studies of beech (Penninckx et al., 1999, 2001; Elhani

Table 3. Regression analysis of the concentration of elements versus time periods of the tree rings (models are presented on Fig. 1)

	model	a	b	c	r ² (%)	p-value
N	a+bX+cX²	57.7502	-0.058955	0.000015	59.93	0.0041
P	a+bX+cX²	8.93568	-0.009133	0.000002	75.69	0.0002
K	a+bX+cX²	98.8608	-0.100717	0.000026	74.90	0.0003
Ca						n.s.
Mg	a+bX+cX²	30.9739	0.031349	7.9·10 ⁻⁵		0.0286
Fe	a+bX+cX²	-1.01836	0.0010253	-2.6·10 ⁻⁷	49.24	0.0240
Mn	a+bX+cX²	-0.779487	0.0008139	-2.1·10 ⁻⁷	57.02	0.0063
Na	a+bX+cX²	5.83874	-0.005983	1.5·10 ⁻⁵	60.71	0.0059
Zn	a+bX+cX²	0.309575	-0.000315	8.0·10 ⁻⁸	53.52	0.0148
Cu	a+bX+cX²	1010.21	-1.03461	0.000265	62.88	0.0026
Pb						n.s.
Cd	a+bX+cX²	-371.191	0.375734	9.4·10 ⁻⁴	75.86	0.0004
Co						n.s.

et al., 2003) and it seems to be determined by physiological processes of translocation of the mobile N fraction in the wood (Poulson et al., 1995). The importance of the translocation was proved by isotope $\delta^{15}\text{N}$ experiment in beech trees (Elhani et al., 2003).

A very similar pattern was noticed for P (Fig. 1). An identical pattern was published by Penninckx et al., (2001) in beech trees of the Belgian Ardennes. However, P concentration in the rings of the beech trees in Mavrovo is much lower than in the case of the Belgian Ardennes. The soil P concentration in Mavrovo (Tab. 1) is about 2 times richer in P than the soil in the Belgian Ardennes. Penninckx et al., (2001) hypothesized that the higher P concentration is a result of the higher efficiency of the trees for utilization of P on poorer soils.

The pattern of K is generally similar to the one of N and P. However, in the case of K the highest con-

centrations were found in the "heartwood". Identical results were reported by Penninckx et al., (2001).

Ca has a different radial pattern than N, P and K. Its concentration either decreases from the pith to the cambium (Penninckx et al., 2001) or has lowest values in both pith and cambium and higher values in the middle-age tree rings (Meisch, 1986; Penninckx, 1999). The decrease of Ca concentration towards the cambial rings is the most probable pattern in the beech trees in Mavrovo. All of the studies on beech trees reported a large variation in Ca concentration. The most important reasons may be the availability of Ca in the soil which decreases in the rainy periods (Penninckx et al., 1999), soil acidification (Penninckx et al., 2001) or industrial emissions (Meisch et al., 1986).

The Mg pattern was very similar to the pattern of K. As already noted, both Mg and Ca showed an increase in the period 1975-1980. This corresponds

Table 4. Regression analysis of the concentration of elements versus climate parameters

	Temperature		Rainfall		Temperature and rainfall	
	r	p-value	r	p-value	r ² (%)	p-value
N	0.49	0.0018	0.03	n.s.	20.17	0.0174
P	0.42	0.0110	0.06	n.s.	16.37	0.0479
K	0.41	0.0089	0.04	n.s.	18.24	0.0241
Ca	-0.25	n.s.	-0.15	n.s.	6.71	n.s.
Mg	0.36*	0.0265	-0.10	n.s.	4.26	n.s.
Fe	-0.11	n.s.	-0.34	0.0342	9.11	n.s.
Mn	0.12	n.s.	0.01	n.s.	1.23	n.s.
Na	0.40	0.0125	-0.19	n.s.	18.42	0.0256
Zn	0.11	n.s.	-0.15	n.s.	8.03	n.s.
Cu	0.37	0.0182	-0.10	n.s.	22.07	0.0099
Pb	-0.17	n.s.	-0.02	n.s.	3.06	n.s.
Cd	-0.08	n.s.	-0.01	n.s.	0.76	n.s.
Co	-0.17	n.s.	-0.05	n.s.	3.07	n.s.

to the lowest values of tree ring widths (unpublished data). In particular, the rings of 1978 showed very low values of tree growth. Thus, the influence of climate and, consequently, the availability of these elements in the soil is the most suitable explanation for the increase of Ca and Mg concentration.

Fe concentration showed a gradual increase from pith to cambium. The highest values in tree #20 were recorded in the period 1975-1980. However, other trees did not show amplitudes in this period. Meisch et al., (1986) ascribed the increase in Fe concentrations in beech tree rings to the pollution in Saarland (Germany).

The Na, Cu and Co radial pattern was very similar to the one of the most important biogenic elements, N and P.

Mn was the only element that showed a gradual decrease from pith to cambium. Both Meisch et al., (1986) and Penninckx et al., (2001) found a very similar pattern. The increase of Mn concentration in Saarland was connected to the periodical emissions (around 1880, before and during the Second World War and in 1960-1970) of smelters in the region (Meisch et al., 1986).

The results of Hagemeyer and Schäfer (1995) show that the zink concentration is highest in the pith and the cambium. It corresponds to the results of our research in Mavrovo (Fig. 1). However, Meisch et al., (1986) recorded a different pattern with the highest values in the middle-aged rings and lowest values in the rings near pith and cambium.

Table 5. Regression analysis of the concentration of elements of individual trees versus climate parameters.

	Temperature				Rainfall				Temperature and rainfall			
	3	14	20	21	3	14	20	21	3	14	20	21
N	○	○	○	○	○	●	○	○	○	○	○	○
P	○	○	●	○	●*	○	●*	○	○	○	○	○
K	●	●	●	○	○	●*	○	○	○	○	●	○
Ca	●	○	●	○	○	○	○	○	○	○	○	○
Mg	○	○	●	○	○	○	○	○	○	○	○	○
Fe	○	●	●	○	○	○	○	○	○	○	○	○
Mn	●*	○	○	○	○	○	○	○	○	○	○	○
Na	●*	●*	○	○	○	○	○	○	○	○	○	○
Zn	○	○	○	○	○	○	○	○	○	○	○	○
Cu	○	○	○	○	○	○	○	○	○	○	○	○
Pb	○	○	○	○	○	○	○	○	○	○	○	○
Cd	○	○	○	○	○	○	○	○	○	○	○	○
Co	○	○	○	○	○	○	○	○	○	○	○	○

It is interesting that Padilla and Anderson (2002) connected higher Cu concentrations in the tree rings of *Pinus ponderosa* with volcanic eruptions in some very distant regions of the world.

The concentration of toxic elements (Cd, Pb) should be low in the cambial area and higher towards the pith. This pattern is a result of the centripetal translocation of toxic elements towards the pith i.e. the tissues with few live cells. The result of this translocation is detoxification of the cambial region and increased amounts of toxic elements in the heartwood (Hagemeyer and Schäfer, 1995). This explanation can be applied in the case of Pb which showed highest concentrations in the pith. However, the radial pattern of Cd does not fit in this explanation. It showed gradual increase of concentration from the pith to cambium.

Table 6. Statistically significant differences (●) and homogenous groups (○) in element concentration in tree rings between four model trees (3, 14, 20 and 21) according to the Fisher's LSD test. Results for Ca, Mg, Fe, Na and Zn are not presented.

	14				20				21			
	3	14	20	21	3	14	20	21	3	14	20	21
N	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
Cu	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
P	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
Pb	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
K	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
Cd	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
Mn	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
Co	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○
	○	○	○	○	○	○	○	○	○	○	○	○

Penninckx et al., (2001) showed that the radial patterns of elements in tree rings are dependent on the plant species. The radial distribution of some elements was found to be completely different in beech and oak (*Quercus robur*) from the same locality.

The comparison of the radial patterns in European beech trees from different localities showed that the radial patterns depend on the local ecological conditions. However, the most important elements (N, P, K, Ca, Mg) have very similar patterns. The differences were noticed in the cases of some micro- and toxic elements (Zn, Cd).

In the case of beech trees in Mavrovo and other regions in Europe the radial patterns can be summarized in the following groups (Taneda et al., 1986 in Penninckx et al., 2001);

- I. The most common pattern (N, P, K) was described by second-order polynomial model with highest values in the pith and cambial region. The

difference in the ratios of concentrations in pith and cambial region should be acknowledged:

- a) In the case of N, P, Na and Cu the highest values were recorded in the cambial region
- b) In the case of K and Zn, the highest values were recorded in the pith

II. Gradual decrease from pith towards the cambium (Mg, Mn, Pb, Co)

III. Gradual increase from pith towards the cambium (Fe, Cd).

The similarity in radial patterns of elements in beech trees from different parts of Europe corresponds to the conclusions of Hagemeyer and Schäfer (1995), Poulson et al., (1995) and Elhani et al., (2003) for the dominant role of the translocation processes in xylem sap in determination of radial patterns of elements. The investigations of Meisch et al (1986), Penninckx et al., (1999, 2001) and in part of Elhani et al., (2003) show that some deviations can be connected to environmental factors (climate, availability, atmospheric pollution and soil acidification).

The influence of climate was probably responsible for the higher values of Ca, Mg and Fe in the tree rings from the period 1975-1980 in Mavrovo.

In general, the radial distribution patterns of elements in tree rings of beech are consistent in different parts of Europe. The most striking similarities were noticed in the case of the most important biogenic elements (N, P, K, Ca) as well as for some micronutrients and heavy metals (Cd, Pb, Zn, Cu). This statement is in accordance with the opinions that the translocation processes in xylem sap are the most important factor in the determination of radial pattern.

Most of the elements have highest concentrations in the outermost tree ring i.e. the cambial region (except for Mg, Mn, Zn, Pb and Co). This type of pattern points to the physiological importance of these elements. The detoxification process that is based on centripetal translocation as the

most important physiological mechanism can explain the increase of the concentration of some heavy metals from the cambium towards the pith.

However, some of the deviations in the concentration values can be explained by the changes in the ecological conditions. In the case of Mavrovo, such deviations must be connected with changes in climatic conditions. Watmough (1999) suggested that chemical analysis of tree-rings may also be used to monitor changes in trace metal deposition remote from point sources. In these studies, however, it is even more critical to understand radial tendencies in wood, so that increases in element concentration in the outer sapwood are not falsely associated with an increase in metal deposition, as often reference or control sites are not available.

The presented radial patterns for the beech trees in Mavrovo can be considered as reference and can be used for comparisons with beech trees in polluted environments. The differences between species, localities and even differences between individual trees from same locality should always be taken into account.

We recorded variation of concentration of the elements among individual beech trees. Also, Nabais et al., (1996) reported that radial distributions of Ni in *Quercus ilex* in Portugal showed large variations among the trees, although they all grew in the same area within a short distance from each other. They postulated that these differences can be caused by small-scale spatial variations in the soil. In the case of Mavrovo, all of the model trees were felled from the same slope of one locality on distance not greater than 50 m. Thus, the explanation of the differences among individual trees should include physiological status of trees, tree height and crown features, differences in throughfall and stemflow chemistry, root development and root competition (especially in mixed stands).

REFERENCES

- Barnes, D., Hamadah, M.A. and J.M. Ottaway, (1976). The lead, copper and zinc content of tree rings and bark. A

- measurement of local metallic pollution. *The Science of the Total Environment* **5**, 63-67
- Bindler, R., Renberg, I., Klaminder, J. and O. Emteryd, (2004). Tree rings as Pb pollution archives? A comparison of $^{206}\text{Pb}/^{207}\text{Pb}$ isotope ratios in pine and other environmental media. *The Science of the Total Environment* **319**, 173-183
- de Vives, A.E.S., Moreira, S., Brienza, S.M.B., Medeiros, J.G.S., Filho, M.T., Zucchi, O.L.A.D. and V.F. Nascimento Filho, (2006). Monitoring of the environmental pollution by trace element analysis in tree-rings using synchrotron radiation total reflection X-ray fluorescence. *Spectrochimica Acta Part B* **61**, 1170-1174.
- Elhani, S., Fernández, L., Zeller, B., Bréchet, C., Guehl, J.-M. and J.-L. Dupouey, (2003). Inter-annual mobility of nitrogen between beech rings: a labelling experiment. *Ann. For. Sci.* **50**, 503-508.
- Fiske, C. F. and Y. Subarow, (1925). The colorimetric determination of phosphorus. *J. Biol. Biochem.* **66**, 375-400.
- Fromm, J., Essiamah, S. and W. Eschrich, (1987). Displacement of frequently occurring heavy metals in autumn leaves of beech (*Fagus sylvatica*). *Trees* **1**, 164-171.
- Glass, G.A. Sr., Hasenstein, K.H., and H.-T. Changm (1993). Determination of trace element concentration variations in tree rings using PIXE. *Nuclear Instruments and Methods in Physics Research* **B79**, 393-396.
- Cutter, B.E. and R.P. Guyette, (1993). Anatomical, chemical, and ecological factors affecting tree species choice in dendrochemistry studies. *Journal of Environmental Quality* **22**, 611-619.
- Hagemeyer, J. and K. Lohrie, (1995). Distribution of Cd and Zn in annual xylem rings of young spruce trees [*Picea abies* (L.) Karst.] grown in contaminated soil. *Trees* **9**, 195-199.
- Hagemeyer, J., Lülfsmann, A., Perk, M. and S.-W. Breckle, (1992). Are there seasonal variations of trace element concentrations (Cd., Pg, Cn) in wood of *Fagus* trees in Germany? *Vegetatio* **101**, 55-63.
- Hagemeyer, J. and H. Schäfer, (1995). Seasonal variations in concentrations and radial distribution patterns of Cd, Pb and Zn in stem wood of beech trees (*Fagus sylvatica* L.). *The Science of the Total Environment* **166**, 77-87.
- Lazarevski, A. (1993). *The climate in Macedonia*. Kultura publishing, Skopje, 282 pp. (In Macedonian).
- Meisch, H.-U., Kessler, M., Reinle, W. and A. Wagner, (1986). Distribution of metals in annual rings of the beech (*Fagus sylvatica*) as an expression of environmental changes. *Experientia* **42**, 537-542.
- Melovski, Lj. and Lj. Grupče, (1999). Station (permanent experimental plot) for complex ecosystem research in beech ecosystem in Mavrovo National Park. *Proceedings of the 1st Congress of ecologists of Macedonia with international participation* **1**, 51-58.
- Nabais, C., Freitas, H. and J. Hagemeyer, (1999). Dendroanalysis: a tool for biomonitoring environmental pollution? *The Science of the Total Environment* **232**, 33-37.
- Nabais, C., Freitas, H., Hagemeyer, J. and S.-W. Breckle, (1996). Radial distribution of Ni in stemwood of *Quercus ilex* L. trees grown on serpentine and sandy loam (umbric leptosol) soils of NE-Portugal. *Plant and Soil* **183**, 181-185.
- Padilla, K.L. and K.A. Anderson, (2002). Trace element concentration in tree-rings biomonitoring centuries of environmental change. *Shemosphere* **49**, 575-585.
- Penninckx, V., Glineur, S., Gruber, W., Herbauts, J. and P. Meerts, (2001). Radial variations in wood mineral element concentrations: a comparison of beech and pedunculate oak from the Belgian Ardennes. *Ann. For. Sci.* **58**, 253-260.
- Penninckx, V., Meerts, P., Herbauts, J., and W. Gruber, (1999). Ring width and element concentrations in beech (*Fagus sylvatica* L.) from a periurban forest in central Belgium. *Forest Ecology and Management* **113**, 23-33.
- Poulson, S.R., Chamberlain, C. P. and A. J. Friedland, (1995). Nitrogen isotope variation of tree rings as a potential indicator of environmental change. *Chemical Geology* **125**, 307-315.
- Tommasini, S., Davies, G. R. and T. Elliott, (2000). Lead isotope composition of tree rings as bio-geochemical tracers of heavy metal pollution: a reconnaissance study from Firenze, Italy. *Applied Geochemistry* **15**, 891-900.
- Watmough, S.A. (1999). Monitoring historical changes in soil and atmospheric trace metal levels by dendrochemical analysis. *Environmental Pollution* **106**, 391-403.
- Watmough, S.A. (2002). A dendrochemical survey of Sugarmaple (*Acer saccharum* marsh) in South-Central Ontario, Canada. *Water, Air, and Soil Pollution* **136**, 165-187.
- Watmough, S. A. and T. C. Hutchinson, (1996). Analysis of tree rings using inductively coupled plasma mass spectrometry to record fluctuations in a metal pollution episode. *Environmental Pollution* **93**, 93-102.
- Watmough, S. A. and T. C. Hutchinson, (1999). Change in the dendrochemistry of sacred fir close to Mexico City over the past 100 years. *Environmental Pollution* **104**, 79-88.
- Watmough, S. A., Hutchinson, T. C. and E. P. S. Sager, (1998). Changes in tree ring chemistry in sugar maple (*Acer saccharum*) along an urban-rural gradient in southern Ontario. *Environmental Pollution* **101**, 381-390.
- Watt, S. F. L., Pyle, D. M., Mather, T. A., Day, J. A. and A. Aiuppa, (2006). The use of tree-rings and foliage as an archive of volcanogenic cation deposition. *Environmental Pollution* **148**, 48-61.

РАДИЈАЛНИ РАСПОРЕД КОНЦЕНТРАЦИЈЕ 13 ЕЛЕМЕНАТА У ПРСТЕНОВИМА БУКВЕ У НАЦИОНАЛНОМ ПАРКУ „МАВРОВО“, РЕПУБЛИКА МАКЕДОНИЈА

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Дендроанализа (дендрохемија) је метод развијен шездесетих година XX века (Hagemeyer and Lohrie, 1995) чији је главни циљ биомониторинг хемијских параметара у животној средини (Meisch et al., 1986; Penninckx et al., 1999).

Овај рад приказује резултате анализе радијалног распореда 13 елемената (N, P, K, Ca, Mg, Fe, Na, Mn, Zn, Cu, Pb, Cd и Co) у прстеновима букве (*Fagus sylvatica* L.) у „незагађеној“ шуми у Националном парку „Маврово“. Добијени распореди показују сличност са другим истраживањима у Европи. Највећи број елемената има највеће вредности концентрација у најактивнијим (камбијалним) прстеновима (са изузетком Pb, Zn, Mn и вероватно Co) што указује на примарни значај физиолошких процеса (особито транслокације) у формирању радијалног распореда. Повећање концентрације тешких метала од камбијума према сржи стабла указује и

на значај детоксификације живих ткива процесом центрипеталне транслокације.

Одступања у концентрацији неких елемената (Ca, Mg и Fe) у периоду 1985-1990 указују и на практични значај који има дендрохемија као историјски архив промена у животној средини. Корелација концентрације у прстеновима са 5-годишњим просечним вредностима температуре и преципитације показала је да концентрација N, P, K, Mg, Na и Cu зависи у првом реду од температуре, а концентрација Fe од годишње преципитације.

С обзиром да је испитивани екосистем под slabим утицајем полутаната, добивени радијални распореди могу се сматрати као резултат унутрашњих физиолошких процеса, а добивена одступања могу се објаснити утицајем климатских фактора.