Macedonian Journal of Ecology and Environment
Vol. XIV (1, 2)
p. 35 - 45
Skopje (2012)
ISSN 1857 - 8330
UDC: 582.632.2-119.2:546.4/.8(497.776)
Original scientific paper

Dendrochemistry of turkey oak (*Quercus cerris*) in iron and manganese mining area

Дендрохемиски истражувања на цер (*Quercus cerris*) во рударски регион за експлоатација на железо и манган

Aleksandar Jankovski[1,*], Ankica Gjorevska[2], Slavcho Hristovski[1] And Ljupcho Melovski[1]

[1]Institute of Biology, Faculty of Natural Sciences and Mathematics,
Ss. Cyril and Methodius University, Skopje, Republic of Macedonia
[2]OSMU D-r Jovan Kalauzi, Bitola

The results of the investigation of radial distribution of some nutrients and heavy metals (Mg, K, Ca, Na, Fe, Cu, Cd, and Mn) in the wood of Turkey Oak (*Quercus cerris* L.) are presented. The goal of the presented work was to analyze the radial patterns of several bioelements and heavy metals as well as to assess the impact of the iron mining and flotation pond. For that purpose, accumulation of above mentioned metals in the tree rings of oak trees in the unpolluted and affected area was analyzed. Several series of tree rings (three consecutive years as an average) were analyzed from the period of active mining (from 1950s to late 1980s). The same analysis was performed in the tree rings in the period after the mining activities were stopped.

Key words: Heavy metals, iron mine, dendrochemistry, *Quercus cerris*

Презентирани се резултати од истражувањето кое се однесува на радијалната распределба на некои нутриенти и тешки метали (Mg, K, Ca, Na, Fe, Cu, Cd и Mn) во дрвесината на церови дрвја (*Quercus cerris* L.). Главна цел беше да се согледаат некои правила во радијалната дистрибуција на некои биоелементи и тешки метали, како и да се воочи влијанието на експлоатацијата на железната руда и нејзината обработка во тек на технолошкиот процес врз содржината на метали во дрвјата. За таа цел, беше анализирана акумулацијата на споменатите елементи во годови од церови дрвја кои беа собрани од незагадени локалитети и од локалитети за кои се смета дека биле под влијание на рудникот .Неколку групации од годови беа анализирани (како просеци од по три години) кои го опфаќаат периодот кога рудникот бил активен (од 1950 година до доцните осумдесетти). Исти такви анализи беа извршени и за периодот по прекинот на експлоатацијата на руда.

Клучни зборови: тешки метали, рудник за железо, дендрохемија, *Quercus cerris*

Introduction

Dendrochemistry (dendroanalysis or biochemical dendrochronology) is an approach based on elements‘ concentration analysis in tree rings. It was developed and used since 1960s with different success. Its practical significance is based on the assumption that the element concentration corresponds to its availability in the period when the tree rings were formed. Dendroanalytical results depend on

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* *aleksandarjankovski@gmail.com*

the wood structure, characteristics of the chemical elements, root absorption and transport in the plant, etc. Physiological processes may influence the tree ring concentration and thus mask the historically determined patterns in the wood and decrease the value of dendroanalysis (Meisch et al. 1986; Hagemeyer & Schäfer 1995; Padilla & Anderson 2002).

Only few dendrochemical studies have been conducted on the Balkan Peninsula (e.g. Georgiev & Raev 1983; Mirchev et al. 2000, 2009; Hristovski & Melovski 2010). There are number of studies, especially in Europe and North America concerning different tree species and various pollution sources (Meisch et al. 1986; Hagemeyer et al. 1992; Hagemeyer & Schäfer 1995; Poulson et al. 1995; Penninckx et al. 1999, 2001, etc).

The main goal of the presented work was to analyze the radial patterns of several bioelements and heavy metals as well as to assess the impact of the iron mining and climate. Accumulation of Mg, K, Ca, Na, Fe, Cu, Cd, and Mn in the wood of Turkey Oak (*Quercus cerris* L.) was analysed, in unpolluted and affected area.

Investigated area

Wood samples were taken from the area of Demir Hisar, south-west parts of the Republic of Macedonia. Two sites were selected: test site and control site (Fig. 1).

Test site (T): within the Demir Hisar Iron Mine (DHIM), on the slopes of the stream flowing below the flotation pond. This site is located on the hill Stavrakovo, on the northeast from the village Sopotnica. The mine is situated at 900-1000 m a.s.l. and covers a surface of approximately 2200 m long by 600-1000 m wide. Mine exploitation started in 1957

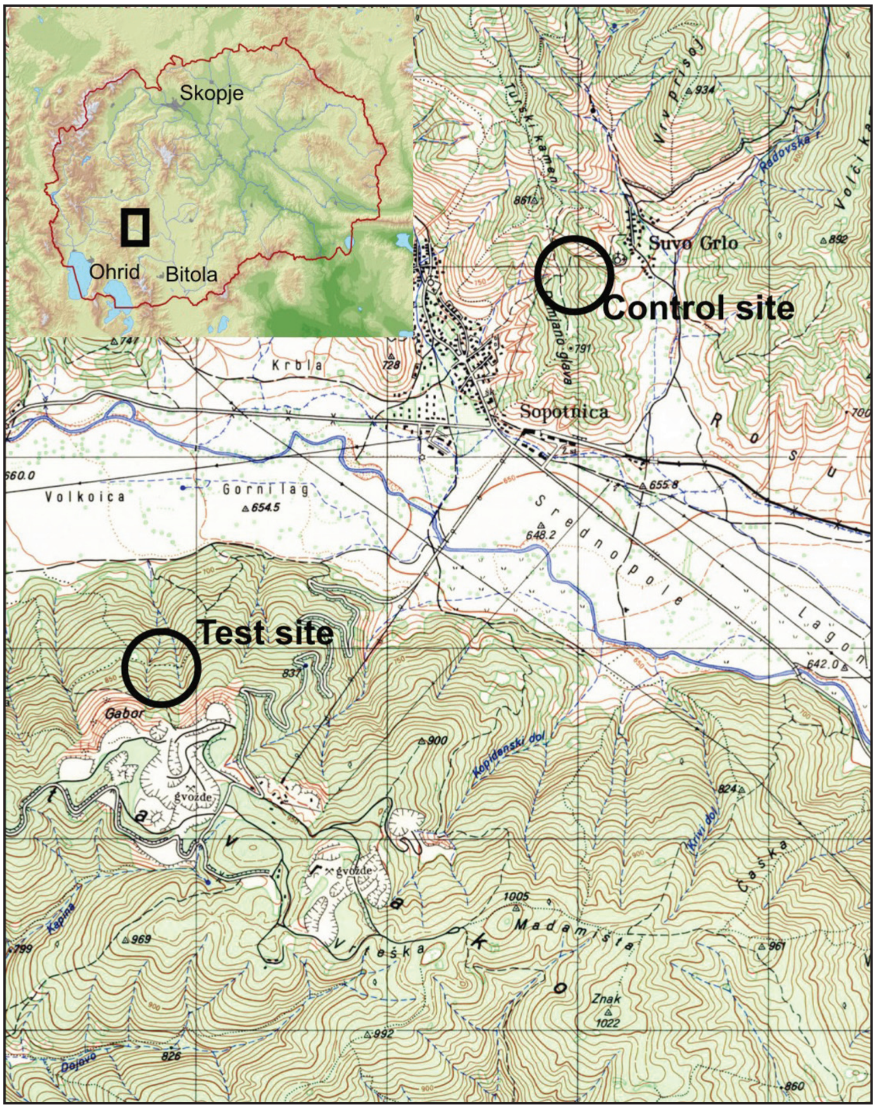

Fig. 1 Geographic location of the investigated area

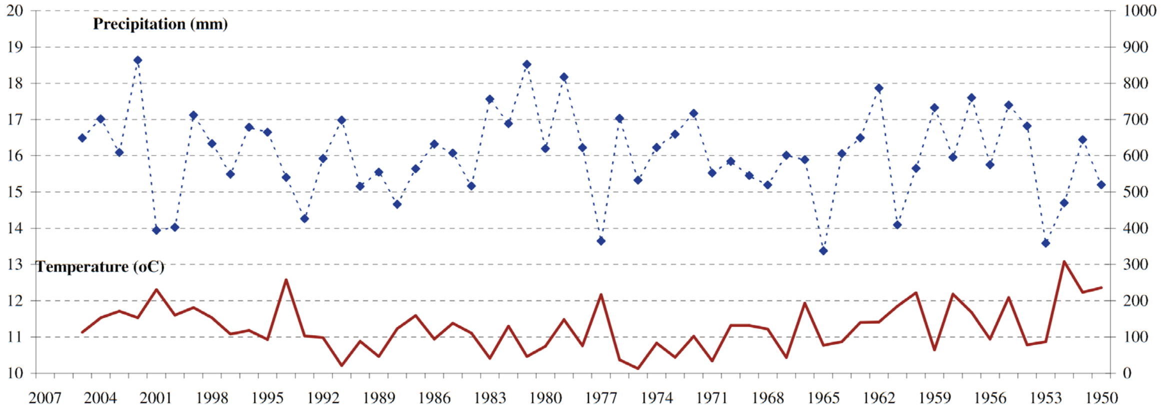

Fig. 2 Mean annual temperatures (left *y*-axis) and annual precipitations (right *y*-axis) in the period between 1950 and 2007, according to the Meteorological station „Bitola”.

by surface quarrying and ore separation. The main ore iron minerals are siderite, limonite and chamosite (Manasiev 1981). The mine closed in 1986. The data on annual ore excavation were found in the archives of the DHIM. These data concerned the period 1957-1986, however the records for the period 1966-1969 were missing.

Control site (C): situated few kilometers from the test site. The locality is situated in the vicinity of village Suvo Grlo. The altitude and environmental conditions were very similar to the test site. The direct impact of the mining activities in the control site was considered insignificant. There are no other polluters in the area of the control site.

Climate

There are no meteorological stations in the investigation area. Thus, the presented climatic characteristics are based on the data for climate of adjacent Pelagonija plain - Meteorological station „Bitola” (Lazarevski 1993). The climate is continental with long and cold winters, short springs and short warm summers.

The average annual temperature of Pelagonija region is 11.2 ^{o}C, with amplitudes of 10.0^{o}C to 13.0 ^{o}C (Fig. 2). The hottest month is June, with an average temperature of 21.8 ^{o}C and the coldest is January with an average of -0.3^{o}C (Lazarevski 1993).

This region has specific orography (vast plain surrounded by mountains), and because of that the annual rainfalls are smaller than the surrounding regions. The average sum of rainfalls is 598 mm per year, with variations from 359 to 818 mm. The most humid month is November with 12% of the annual average, and the most arid month is August with 6% of the annual average.

The most humid season is autumn with average sum of 171 mm, or 29% of the yearly average, and the most arid is summer with 116 mm or 18% of the annual average. In the region of Pelagonija there are 119 rainy days annually. The snowfalls are the most common in the period from October to April, but the most frequent snowfalls are noticed in the period of January, February and March with maximum range from 60 to 65 cm snow cover (Lazarevski 1993).

The dry periods are very common in this region, mostly like short dry periods with duration from 10 to 15 days in the summer months, but dry periods of up to 60 days are also common. Winds have local character with low velocity. The most frequent winds are those from north and south direction.

Geology and soil characteristics

The geological substrate in DHIM is rich in minerals, especially iron, but the presence of other heavy metals is also important (lead, zinc, barium, nickel, cobalt, vanadium, copper, chromium) (Manasiev 1981). It is important to notice that the concentration of elements varies in different ore layers: in some layers they can be found in high concentrations, and in some layers they can be completely absent (Manasiev 1981). The main iron ores are limonite, siderite, magnetite, and chamosite in small quantity.

The soils in Demir Hisar region are of alluvial or delluvial origin, mostly formed by river Crna Reka alluvial deposits and other rivers in this region. The main soil type in the investigated oak forest is brown forest soil (cambisol) according to the FAO soil classification system (Filipovski 2006).

Materials and methods

Six Turkey oak trees (*Quercus cerris* L.) were selected during February 2007, out of which 3 were test samples (T), and the other 3 control samples (C). All of the samples were treated by the same methods (field work and laboratory analyses). During the field work we cut down tree discs (5 cm thick) from each tree at breast height.

We smoothed disc surfaces by hand polishing in the laboratory. Tree ring width was then measured using stereomicroscope MBS-10 (Lomo, Sanct Petersburg) and ocular scale (magnification of X56). Tree ring width for each ring was measured in four directions (north, east, west and south) and average values were calculated (Bräker 1996), also in order to avoid mistakes each tree ring was marked, and on each disc the tree rings was counted up starting from the youngest to the oldest. Cross-dating was performed by matching patterns of wide and narrow rings between discs of all six trees.

We calculated the growth index (*i*) which is relation between the measured width of the tree rings (W) and the G (expected) value. G value was calculated on the base of the five-year averages (average of tree ring widths: n-2, n-1, n, n+1, n+2) of tree rings widths (Fritts 1976; Mirchev et al. 2000). This gave better results than calculating of a G values based on polynomial regression analyses that eliminated most of the growth signals (Mirchev et al. 2000).

Chemical analyses were performed on the wood of tree rings from each of the six tree discs. Each Separate annual tree rings were extracted and analyzed from trees C-II and T-II. Tree rings in groups of 3 were extracted from trees C-I, T-I and T-III. In the case of tree C-III, we have taken samples in groups of 5. The samples were taken in groups of 3 due to the narrow rings of the trees (or 5 in the case of C-III because of the very narrow rings). In total, 119 test samples were prepared. Each sample contained wood parts from four sides of the trees disc. The samples were grinded in electric mill and dried.

Wet digestion of the material was used for determination by atomic absorption spectrometry of heavy metals in the tree rings (Allen et al. 1989). Approximately, 1 g dry mass was digested in 10 ml of digestion solution (HNO_3:$HCLO_4$:H_2SO_4=10:2:1). Digested samples were transferred in 25 ml flasks thorough filter paper with hot distilled water. The samples were stored in plastic tubes in freezer at 4 °C. Three blind samples were prepared following the same procedure (without woody material). The measurement of the concentration of metals in the samples was made by atomic absorption spectrometry on Varian AAS 10BQ. We calculated the concentrations of each element using the formula:

$$\gamma = \frac{c \cdot V - S}{m}$$

where:

γ - concentration of the element in the tree ring wood ($mg \cdot kg^{-1}$);
c - concentration in test tubes from AAS measurements ($mg \cdot l^{-1}$);
V is volume of the flask (25 ml);
S - average concentration of the element in the blind samples ($mg \cdot l^{-1}$);
m - dry mass of the tree rings (g).

Results

Dendrochronology

The oldest among the test trees was T-III with 36 years, and other two (T-I and T-II) were 35 years old. Among the control trees the oldest tree was C-III with 58, then C-II with 37, and C-I with 33 years. The number of tree rings measured at breast height does not shows the exact tree age, but it is about ten years lower (Rosaz 2003).

T-III showed the lowest values for *i*, especially

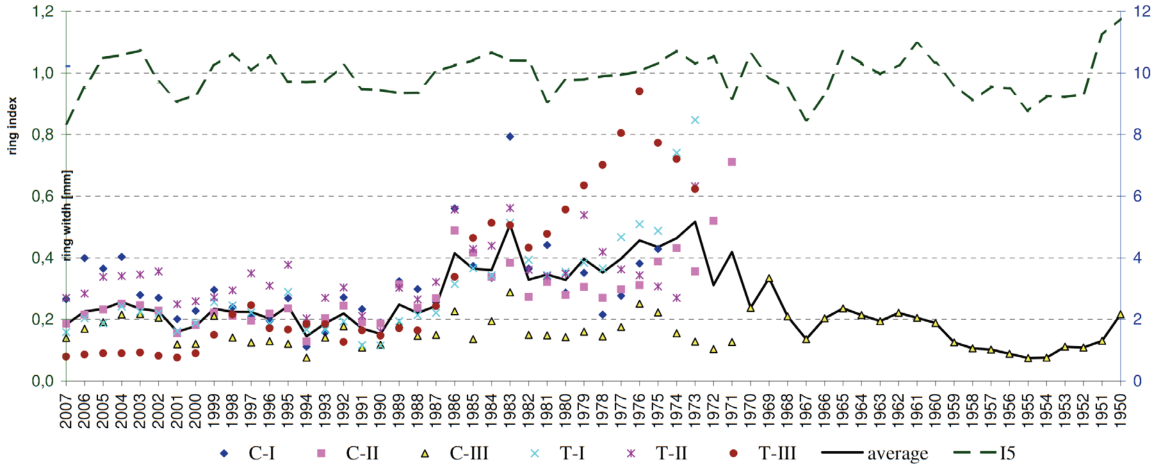

Fig. 3 Tree rings widths of investigated trees (at breast height), test and control trees between 1950-2007 (right y axis) and growth index (left y axis).

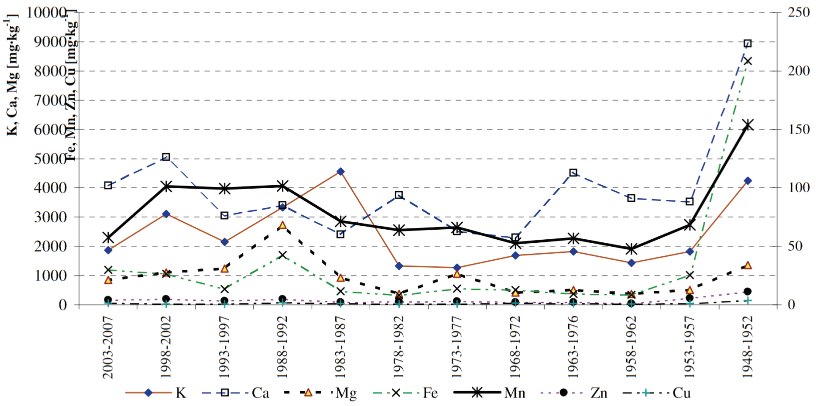

Fig. 4 Radial distribution of heavy metals in the tree rings of *Quercus* cerris C-III near the Demir Hisar iron mine (values for K, Ca and Mg on left *y*-axis, values for Fe, Mn Zn and Cu on right *y*-axis).

in the period between 1972 and 1994.The most extreme values were observed in C-III, with intensive growth between 1973 and 1981, and the highest values in 1976. C-I had intensive growth in 1973and 1974.The other trees had small variations (with some exceptions) compared to the average tree rings width. C-III (the oldest tree) had low growth in the early 1950s and 1960s, until 1967. In the 70s and 80s of the 20th century, all trees had more intensive growth, which decreased in the 90s (Fig. 3).

4.2. Dendrochemistry

Distribution patterns of elements' concentrations (K, Ca, Mg, Fe, Mn, Zn, Cu) are presented on

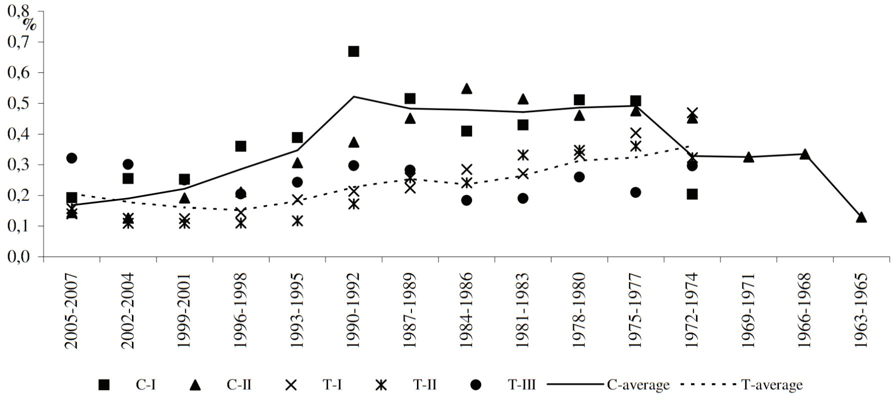

Fig. 5. Radial distribution of potassium in the tree rings of *Quercus cerris* control (C) and test trees (T) near the Demir Hisar iron mine.

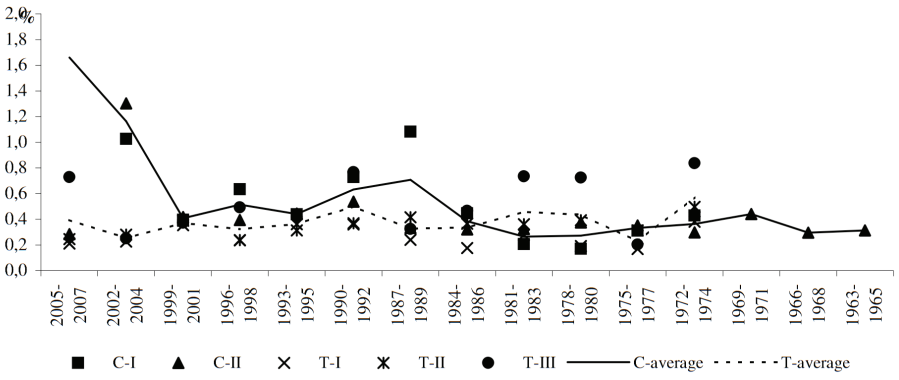

Fig. 6. Radial distribution of calcium in the tree rings of *Quercus cerris* control (C) and test trees (T) near the Demir Hisar iron mine.

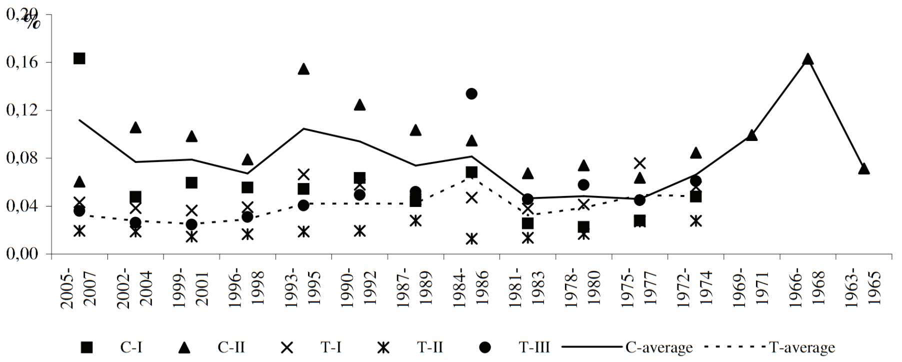

Fig. 7. Radial distribution of magnesium in the tree rings of *Quercus cerris* control (C) and test trees (T) near the Demir Hisar iron mine.

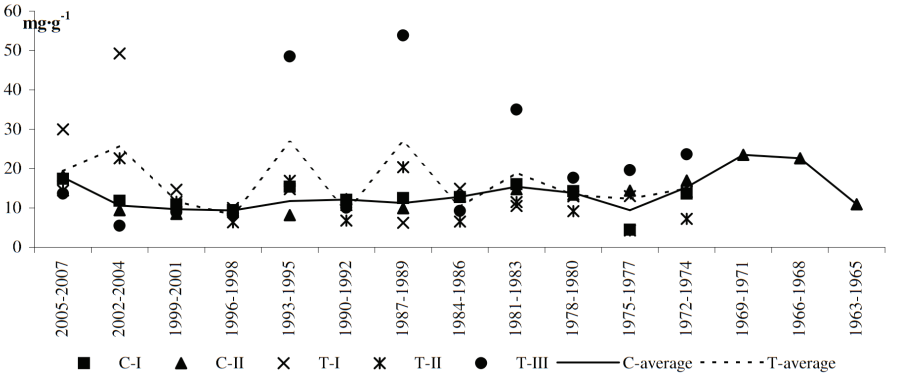

Fig. 8. Radial distribution of iron in the tree rings of *Quercus cerris* control (C) and test trees (T) near the Demir Hisar iron mine.

separate graphs (Figs. 4-11). Only in the case of C-III, all of the elements are presented simultaneously (Fig. 4).

The highest values of all elements were recorded in the oldest rings of C-III (Fig. 4). High values for all of the elements were noticed in the periods 1988-1992 and/or 1998-2002.

Tab.1 Statistical parameters of the analysis of the polynomial models applied for the relation between concentrations and tree ring age of the test and control trees (C-III excluded) near the Demir Hisar iron mine.

Element	p	R^2 (%)	F	n
K-C	0.0000	85.73	36.05	15
K-T	0.0000	91.38	47.70	15
Ca-C	0.0009	68.87	13.27	15
Ca-T	0.0536	51.87	4.31	14
Mg-C	n.s.			
Mg-T	n.s.			
Fe-C*	0.0027	65.8	10.59	14
Fe-T	n.s.			12
Mn-C	0.0429	40.83	4.14	15
Mn-T	0.0034	71.68	11.39	12
Zn-C*	0.0644	39.26	56.14	14
Zn-T	0.0009	78.86	16.78	12
Cu-C	0.0523	38.84	3.81	15
Cu-T	0.0189	58.13	6.25	12

* The extreme values for the period 1963-1965 were excluded.

Potassium. The highest K concentrations were recorded in the period of 1957-1992 (Fig. 5). The lowest concentrations are present in the core and cambial rings. The concentrations in test trees was lower than the concentration of control trees (t-test: $p<0.05$).

Calcium. The highest Ca concentrations were observed in the youngest (cambial) tree rings (Fig. 6). There was no statistically significant difference between the values of test and control trees.

Magnesium. Mg concentration in control trees was significantly higher compared to the test trees ($p<0.05$) (Fig. 7). This difference is due to the high values of Mg concentrations in C-II. There is no obvious trend of Mg accumulation in old or young annual rings (Tab. 1).

Iron. The highest Fe concentrations in the test trees were noticed for T-III in the periods 1981-1983, 1987-1989, 1993-1995 and 2002-2004 (Fig. 8). Generally, the test trees had higher Fe concentrations than control trees. However, the t-test showed no significant differences between the average val-

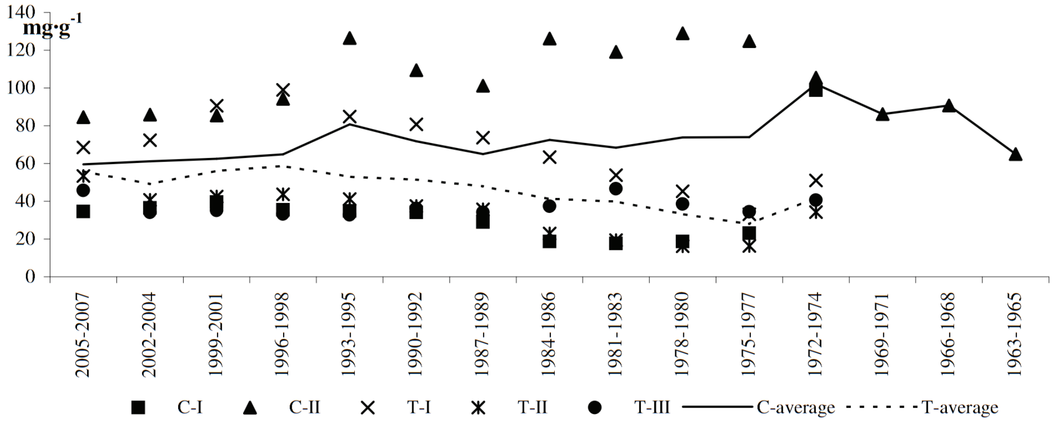

Fig. 9. Radial distribution of manganese in the tree rings of *Quercus cerris* control (C) and test trees (T) near the Demir Hisar iron mine.

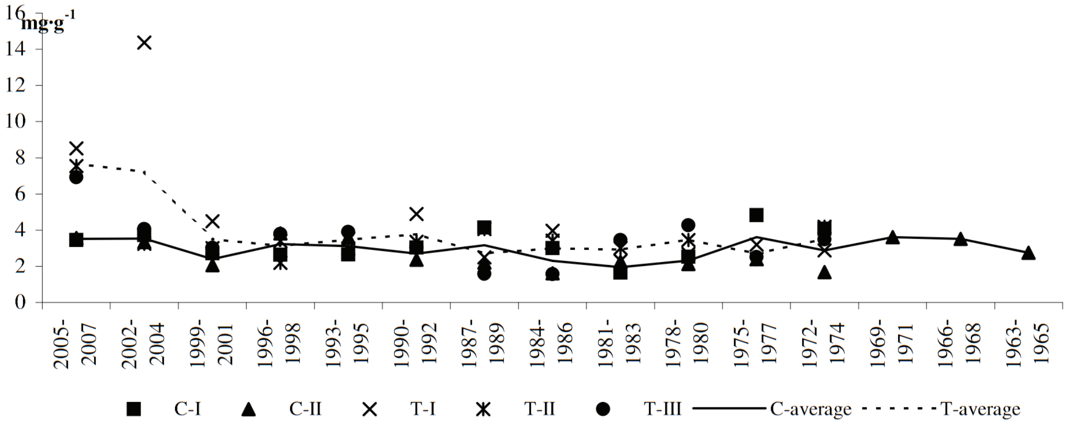

Fig. 10 Radial distribution of zinc in the tree rings of *Quercus cerris,* test (T) and control (C) group of trees near the Demir Hisar iron mine.

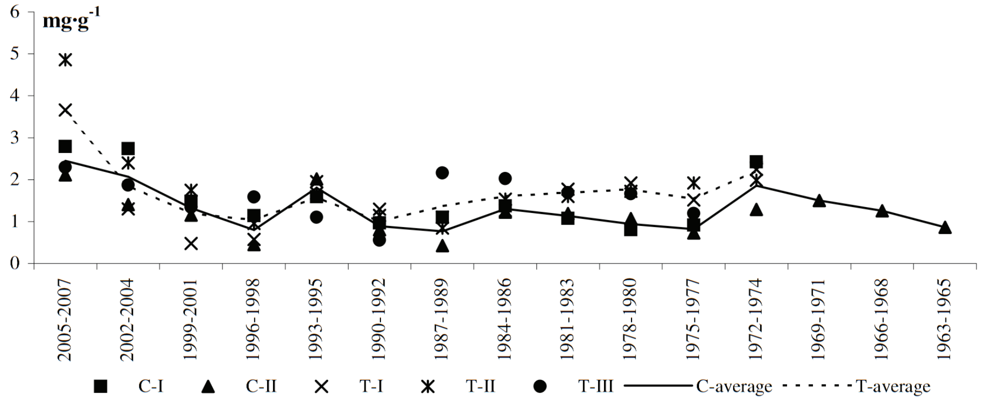

Fig. 11 Radial distribution of copper in the tree rings of *Quercus cerris*, control trees (C) and test trees (T) near the Demir Hisar iron mine.

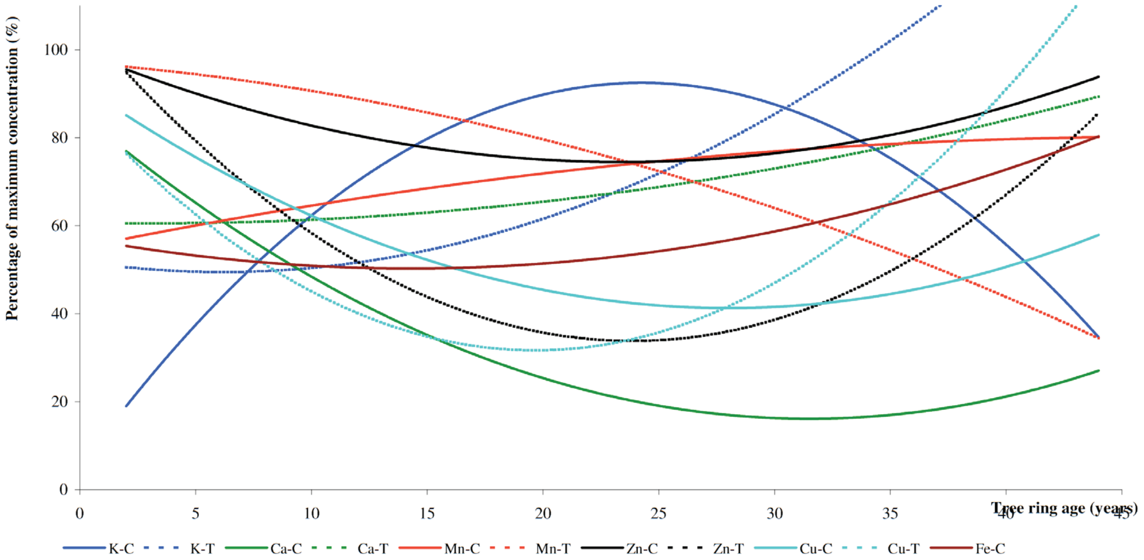

Fig. 12 Second order polynomial models of the radial distribution of heavy metals in the tree rings of *Quercus cerris* in control (C) and test (T) groups of trees in Demir Hisar iron mine.

ues of Fe concentration in test and control trees ($p>0.05$).

Manganese. The statistical analysis (t-test) showed significant difference ($p<0.05$) between control and test trees, and this is because of the very high values measured in C-II. (Fig. 9)

Zinc. The zinc values showed very small variations within the test and control groups. Test trees had higher values the control trees. The statistical analysis (t-test) proved significant difference between test and control trees ($p<0.05$) (Fig. 10)

Copper. Variations of concentrations in control and test trees are very similar, i.e. the periods with high and low concentrations in control and test group mostly overlap (Fig. 11). The results from the statistical analysis (t-test), showed that the test group had higher values for copper than the control trees ($p<0.05$).

Physiological and climate factors

Polynomial equations are the best fit models to describe the radial distribution patterns of the concentration of the analyzed elements in tree rings. Mainly, the highest concentrations of metals are present in the oldest or the youngest tree rings, and the lowest in the physiologically inactive wood. In most of the cases, this pattern is statistically significant $p<0.05$ (Tab. 1).

Only potassium and manganese represent exceptions. The lowest values for Mn concentration were noticed in the oldest tree rings (hard wood) in test trees and in the youngest tree rings in control group (Fig. 12).

Regression analysis for the relation between the concentration of the elements and mean annual temperature and the precipitation showed significant relationships ($p<0.05$) only for:

- Mg concentration in the test group and the average temperature, positive correlation and
- Fe concentration in the control group and the annual rainfall, negative correlation.

Discussion

The highest growth rates were recorded in the period of 80s and 90s of the 20th century. The main reasons for these amplitudes are various ecological factors, which affected the trees during their growth, thou in some cases, the period and the type of mine exploitation can also have significant impact (Bräker 1996). Cherubini et al. (2003) had very similar results for the tree rings growth of Turkey oak from Lajatico (Toscana, Italy). They found higher growth values in the period of of 80s and 90s of the 20th century also followed by decrease afterwards. The higher growth of the forests in the last two decades of 20th century was also noticed in different parts of the World, for different tree species (e.g. Biondi 1999 for *Pinus ponderosa* in USA; Feliksik & Wylczynski 2003 for *Pseudotsuga menziesii* in Poland). According to Briffa et al. (1998), the whole 20th century is known for high and intensive tree growth, probably because of the global human (mainly climate) impact. However, the impact of the ecological factors depends on the age of trees. In general, younger trees and forest stands are more sensitive (Bascietto et al. 2004), and the growth intensity is slowing as the trees are growing older (Ivanovski and Ristevski 1986; Briffa et al. 1998). Older trees in DHIM had also slower growth rates.

In general, the highest values for the concentration of heavy metals were noticed in the oldest tree rings (pith), then in the cambial rings, and the lowest values in the middle-aged tree rings (Fig.12). Some deviations from this pattern can be found in the literature: Wathmough & Hutchinson (1996) noticed the highest concentrations of Zn, Cu, Fe, and Mn in the youngest tree rings of *Acer pseudoplatanus* near Liverpool, England; Nagj et al.(1987) found higher values for Zn, Fe and Mn in the youngest tree rings of *Quercus cerris*, and for the Cu, S, V, Pb in the oldest tree rings; Pennickx et al. (2001) found higher values for Mn in the youngest tree rings of *Quercus robur* in the Ardens in Belgium, etc.

In our case, there were individual variations (Fig. 12). Control group had the highest values in the oldest rings (the core), while the test group showed highest concentration values in the youngest tree rings. Very similar results were reported by Hristovski & Melovski (2010) for the beech forest trees, from National Park Mavrovo, especially in the case of Zn and Fe.

The radial distribution of the elements, in the tree rings of different tree species is mainly a result of the processes of xylem translocation (Hegemeyer and Schäfer 1995; Poulson et al. 1995; Elhani et al. 2003). Meisch et al (1986), Penninckx et al. (1999, 2001) and partly Elhani et al. (2003) proposed that some variations can be attributed to the ecological factors (climate, air pollution, soil acidity, mineral maters accessibility). However, the rainfall and the temperature had insignificant impact on the distribution of the measured elements in the tree rings in DHIM, except in two cases. Hristovski and Melovski (2010) found very significant relation between the temperature and rainfalls, and the radial distribution of elements in beech trees.

One should be careful when ascribing the differences of elements' content in the test and control groups of trees to the pollution effect of the iron mine because the two groups grow in different ecological conditions although the climate does not have significant impact. For Zn and Cu we found higher values in the tree rings of the test trees compared to the control group. These results indicate that iron mine had some impact. However, in the case of K, Mg and Mn we noticed that the values are higher in the control group of trees. Nagj et al. (1987) had similar conclusions during their research on *Pinus* sp. near the thermo-electric power plant (Istra, Croatia). They classified the elements into three groups:

1. A group of elements whose concentrations has increased after the start up of the power plant. This group includes (S, V, Cr, Cu and P).
2. The elements that were not affected by the plant operation, this group includes elements (K and Ti).
3. The third group includes elements (Ca, Mn, Fe and Zn) whose concentrations decreased in comparison with older rings.

Mining activities impact on *Pinus ponderosa* was studied by Sheppard & William (1975, in: Padilla & Anderson 2002). They concluded that chromium concentration was correlated to the mining intensity.

Statistical analyses showed no obvious relationship between annual ore production in the DHIM and elements' concentrations in the tree rings. Only in the case of Mg in T-II there was strong correlation between the concentration and annual ore production according to the simple regression model (Fig. 13). The Mg concentration in tree rings increased with the ore production ($p<0.05$). The case of Mg shows that the impact of DHIM on tree ring

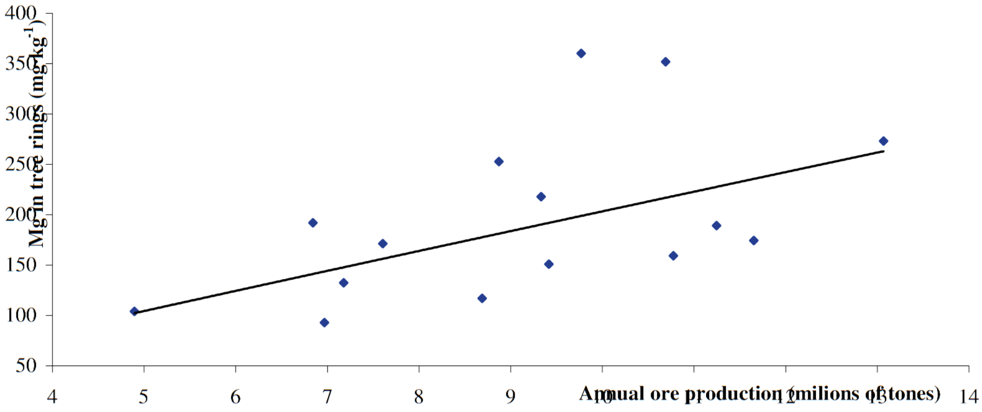

Fig. 13 Simple linear regression model of the relationship between Mg concentration in the tree rings of T-II (Turkey oak) and annual ore production of the Demir Hisar iron mine ($p<0.05$).

radial patterns of individual elements might be expected. However, only 15 pairs of values were analyzed because of the insufficient information on ore production, as well as due to the small age of the test trees.

Dendrochronological results showed that the periods of the 80s and 90s of XX century are characterized by higher growth of trees. Dendrochemical analyses showed that Cu and Zn concentration in the test group tree rings is higher compared to control trees, while K, Mg and Mn showed higher values in the control group. The radial distribution of the elements was determined by the trees physiology. Temperature and rainfalls have no significant influence on the radial distribution of heavy metals in the tree rings. Positive correlation was proved for Mg concentration in the tree rings and annual ore production in the Demir Hisar iron mine suggesting that mining activities might have broader impact on the trees dendrochemistry.

References

Bascietto, M., Cherubini, P. and Scarascia-Mugnozza, G. (2004). Tree rings from a European beech forest chronosequence are useful for detecting growth trends and carbon sequestration. *Canadian Journal of Forest Research*, **34**: 481-492.

Biondi, F. (1999). Comparing tree-ring chronologies and repeated timber inventories as forest monitoring tools. *Ecological Applications,* **9(1)**: 216-227.

Bräker, O. U. (1996). Tree-ring growth trends since the Swiss forest damage inventory “Sanasilva 1984”: results of a 1992 pilot study. In: Dean, J. S., Meko, D. M., Swetnam, T. W. (eds.). Radiocarbon 1996. *Tree rings, environment and humanity*. 363-370.

Briffa, K. R., Schweingruber, F. H., Jones, P. D., Osborn, T. J., Harris, I. C., Shiyatov, S. G., Vaganov, E. A., Grudd, H. (1998). Trees tell of past climates: but are they speaking less clearly toady? *Phil. Trans. R. Soc. Lond.*, **B 353**: 65-73.

Cherubini, P., Gartner, B. L., Torgnetti, R., Bräker, O. U., Schoch, W., and Innes, J. L. (2003). Identification, measurement and interpretation of tree ring in woody species from Mediterranean climates. *Biol. Rev.,* **78**: 119-148

Elhani, S., Fernández, L., Zeller, B., Bréchet, C., Guehl, J.-M., Dupouey, J.-L. (2003). Inter-annual mobility of nitrogen between beech rings: a labelling experiment. *Ann. For. Sci.,* **50**: 503-508.

Feliksik, E., Wylczynski, S. (2003). Tree rings as indicators of environmental change. Electronic Journal of Polish Agricultural Universities, *Forestry,* **6(2)**: 1-8.

Fritts, H. (1976). Tree rings and climate. Academic Press, London

Georgiev, N, S., Raev, I. T. (1983). Possibilities for investigation the history of the changes in the radial growth of forests from Fagus sylvatica L. by tree ring analysis. Third National Conference of Botany, Sofia 26-30.10.1981. Publishing House of the Bulgarian Academy of Sciences, 511-618 (in Bulgarian).

Hagemeyer, J., Lulfsmann, A., Perk, M., Breckle, S.-W. (1992). Are there seasonal variations of trace element concentration (Cd., Pb, Cn) in wood of Fagus trees in Germany? *Vegetatio,* **101**: 55-63.

Hagemeyer, J., Schäfer, H. (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 Evironment,* **166**: 77-87.

Hristovski, S., Melovski, Lj. (2010). Radial patterns of 13 elements in the tree rings of beech trees from Mavrovo National Park, FYROM. Arch. Biol. Sci., Belgrade, **62(2)**: 351-361.

Ivanovski, C., Ristevski, P. (1987). The development and increment of intact beech forest in Osogovo. Journal of Forestry **1-5**: 23-39 (in Macedonian).

Lazarevski, A. (1993). The climate in Macedonia. Kultura publishing, Skopje, 282 pp. (in Macedonian).

Manasiev, J. (1981). Metalogeny of iron and resources of the Demir Hisar mining area. Master Thesis, University in Belgrade (in Serbian).

Meisch, H.-U., Kessler, M., Reinle, W., Wagner, A. (1986). Distribution of metals in annual rings of the beech (Fagus sylvatica) as an expression of environmental changes. *Experientia*, **42**, 537-542.

Mirchev, C., Lyubenova, M., Chikalaniov, A., Simeonova, N. (2000). *Dendrochronology - a short course*. Pensoft PH, Sofia-Moscow, 198 p. (in Bulgarian).

Mirchev, C., Lyubenova, M., Dimitrova, V. Bratanova-Doncheva, S. (2009). Dendrochronological investigation on *Castanea sativa* Mill. in Belasitza Mountain and Western Balkans (Berkovitza Mountain). *Biotechnol. & Biotechnol*. EQ. 23/2009/SE. XI Anniversary scientific conference. 120 Years of academic education in biology. 45 Years faculty of biology.

Nagj, M., Injuk, J, Valković, V. (1987). Trace element concentration variations in tree rings. *Nuclear Instruments and Methods in Physics Research*, **B22**: 465-472.

Padilla, K. L., Anderson, K. A. (2002). Trace element concentration in tree-rings biomonitoring centuries of environmental change. *Shemosphere,* **49**: 575-585.

Penninckx, V., Glineur, S., Gruber, W., Herbauts, J., Meerts, P. (2001). Radial variations in wiood 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., Gruber, W. (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., Friedland, A. J. (1995). Nitrogen isotope variation of tree rings as a potential indicator of environmental change. *Chemical Geology,* **125**: 307-315.

Rozas, V. (2003). Regeneration patterns, dendroecology, and forest-use history in an old-growth beech-oak lowland forest in Northern Spain. *Forest Ecology and Management*, **182**: 175-194.