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Tree ring analysis of *Pinus heldreichii* used to detect amounts and changes of mineral pollution in the northern Pirin mountains, Bulgaria

Abstract

Yurukova, L.: Tree ring analysis of *Pinus heldreichii* used to detect amounts and changes of mineral pollution in the northern Pirin mountains, Bulgaria. – *Bocconea* 5: 473-476. 1997. – ISSN 1120-4060.

Macro- and microelements (N, P, K, Ca, Mg; Fe, Na, S, Al, Mn, Zn, Cu, Pb, Cd, Co, Ni, Ba, Sr) in dated 20-year segments of wood and total bark of *Pinus heldreichii* have been quantitatively analysed in 5 trees c. 90 years old. The distribution pattern of elements in the tree ring segments and the reduction of growth rate with age are discussed.

Introduction

The Mediterranean species *Pinus heldreichii* Christ grows naturally in Albania, Bulgaria, Greece, Italy, and the former Federal Republic of Yugoslavia (Papaioannou 1975). The largest stands of this tertiary relic in Bulgaria stock in the northern Pirin mountains. This pine species, subendemic to the Balkan Peninsula, has been the subject of studies of its phytogeographical relations, ecological peculiarities, and the above-ground productivity of its communities (Paskov 1932; Stefanov 1943; Stojanov 1950; Penev 1966; Radkov 1973; Garelkov & Georgiev 1975; Velčev 1981, etc.). A phytocoenological investigation (Velčev & Vasilev 1987) was made to study its ecology and the factors limiting its spread in the northern part of Mt Pirin; it examined the conditions of its development, the composition, structure and peculiarities of its communities, their syndynamics and their changes under the influence of anthropogenic factors.

The present study reports concentrations of macro- and microelements in *Pinus heldreichii* trunks as well as their changes during the trees' growth.

Table 1. Macroelement concentrations ($\text{mg} \cdot \text{g}^{-1}$) in *Pinus heldreichii* wood (by segments of 20 annual tree rings) and bark (total); averages from 5 trees.

Element	< 1911	1912-1931	1932-1951	1952-1971	1972-1991	bark	bark / rings
N	0.3±0.1	0.3±0.1	0.5±0.1	0.5±0.2	0.6±0.2	3.2±1.0	7.3
P	0.01±0.003	0.01±0.004	0.02±0.004	0.07±0.02	0.10±0.03	0.12±0.04	1.7
K	0.18±0.06	0.21±0.07	0.25±0.08	0.38±0.13	0.40±0.12	0.54±0.16	1.9
Ca	0.92±0.26	0.89±0.25	0.86±0.19	0.74±0.21	0.58±0.14	11±4	14.0
Mg	0.23±0.06	0.23±0.07	0.24±0.07	0.22±0.06	0.18±0.05	0.25±0.07	1.1

Table 2. Microelement concentrations ($\text{mg} \cdot \text{kg}^{-1}$) in *Pinus heldreichii* wood (by segments of 20 annual tree rings) and bark (total); averages from 5 trees.

Element	< 1911	1912-1931	1932-1951	1952-1971	1972-1991	bark	bark / rings
Fe	36±11	34±10	43±13	82±26	145±44	223±73	3.3
Na	64±21	69±20	74±24	93±29	111±36	58±18	0.7
S	61±19	68±21	75±23	93±28	115±37	225±70	2.7
Al	7.2±2.2	11±3	13±4	19±6	26±8	244±78	16.0
Mn	3.4±1.0	4.1±1.1	4.2±1.2	5.3±1.6	9.1±2.9	7±2	1.3
Zn	4.1±1.4	4.4±1.5	5.2±1.5	5.4±1.6	6.5±1.9	15±4	2.9
Cu	0.10±0.02	0.11±0.03	0.10±0.03	0.11±0.03	0.12±0.04	1.4±0.4	13.0
Pb	0.48±0.14	0.62±0.20	1.1±0.3	2.3±0.8	2.2±0.7	6.1±1.9	4.7
Cd	<0.01	<0.01	<0.01	<0.01	<0.01	0.01±0.002	
Co	0.01±0.003	0.01±0.003	0.01±0.002	0.02±0.003	0.02±0.004	0.08±0.02	8.0
Ni	1.1±0.3	1.4±0.4	1.5±0.4	3.3±0.9	1.9±0.5	0.41±0.12	0.2
Ba	0.61±0.19	0.69±0.21	0.64±0.20	0.88±0.28	0.66±0.22	5.4±1.7	7.7
Sr	0.70±0.23	0.73±0.24	0.87±0.28	0.89±0.29	0.73±0.23	5.5±1.6	7.1

Materials and methods

The samples were collected in a locality in the northern Mt Pirin (41°49'44"N, 23°23'17"E, alt. 1780 m, slope 30°, NW exposure). Five *Pinus heldreichii* trees were selected from a monodominant community on marble. They were 83, 84, 86, 88, and 92 years old, respectively. The mean trunk diameter was 28.4 cm, and the mean height, 20.2 m. An increment core, of 0.7 mm in diameter and above 20 cm in length, was taken from each of the five trees with a Pressler borer, from the NW, at breast height (1.3 m). Each wood core was divided into 20-year segments, the bark portion remaining undivided. The wood samples were dry ashed at 500°C. The ash was dissolved in 10 ml 20 % hydrochloric acid and heated on a sand bath to about 120°C to near dryness. The filtrate was diluted with double distilled water to 25 ml. Analyses for the elements P, K, Ca, Mg, Mn, Fe, Na, S, Al, Cu, Zn, Pb, Cd, Co, Ni, Ba and Sr were made by inductively coupled plasma (ICP-AES), using standard determination (Cresser & al. 1991). Nitrogen was analysed according to the Kjeldahl method. The growth rates were estimated from the length of the segments. In order to avoid error due to shrinkage from loss of moisture, the oven-dry length was used (Kozłowski 1971).

Results and discussion

The macro- and microelement concentrations in the wood and bark clearly differ (Tables 1-2). The average content for the wood is, in descending order: Ca > N > K > Mg > Na > S > Fe > P > Al > Mn > Zn > Ni > Pb > Sr > Ba > Cu > Co > Cd; while for the bark it is: Ca > N > K > Mg > Al > S > Fe > P > Na > Zn > Mn > Pb > Sr > Cu > Ni > Co > Cd. The ratios between the concentration in the bark and the average concentration in the wood core segments vary from 0.2 for Ni to 16 for Al. The concentration in the wood of P, Fe, Al, Mn, Na, S, N, K and Zn has increased during the last decades. The Ca amount increases from the younger to the older wood segments. The metals Ni, Pb, Ba and Sr show an increased concentration between 1952 and 1971. There is a significant difference in lead content in wood formed during the last 40 years when compared with pre-1952 values.

There are three pathways by which elements enter a tree: uptake from the soil by the roots, foliar uptake, and direct deposition onto the stem surface followed by lateral diffusion across the bark and into the wood. In addition, many elements show a characteristic horizontal and vertical distribution pattern within tree trunks (see e.g. Martin & Coughtrey 1982, Symeonides 1979).

A decrease in growth with age, i.e., reduction in annual ring width, is normal for tree species (Robitaille 1981, Thompson 1981). We found that between 1911 and 1931 the growth has decreased at a mean rate of 0.13 units per year, then at rates of 0.06, 0.05, and 0.05 units per year between 1932-1951, 1952-1971, and 1972-1991, respectively.

In summary, one may conclude that the data obtained reflect a comparatively low degree of pollution, and but slight reduction in growth with age of the trees studied. It would be interesting to compare these results with those from *Pinus heldreichii* of other localities, and from other coniferous species.

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