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UTILIZATION AND ACCUMULATION OF Zn AND Mn IN QUERCUS FRAINETTO PHYTOMASS IN DIFFERENT REGIONS IN BULGARIA

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ABSTRACT

Ljubenova, M. (1997). Utilization and accumulation of Zn and Mn in Quercus frainetto phitomass in different regions of the country. Ecol. Zast Sred., Vol. 5, No. 1. Skopje.

The acauntment of Zn and Mn in *Quercus frainetto* Ten. model trees has been studied. This research was done by the method of the atomic absorption in .3 different fractions of phytomass-leaves, annual branches and wood. The model trees have been chosen from 3 parts of the country: Kamchia mountain, Sarnena gora and the north-east parts of Rodopa mountain.. There has been done a dendrological analysis of the acauntment.

The aim of this research is to study the biological accumulation, utilization and the correlative dependence between the acauntment of these vitally indispensable trace elements. As a result of the analysis some interesting regularities have been determined. It was found that Zn is accumulating predominantly in the wood and Mn - manely in the annual branches and leaves, which is connected with the content of this elements in the soil. There has been observed a directly proportional for Zn and inversely proportional for' Mn dependence between the average acauntment of the elements in the phytomass fraction and the age of the forest. The dendrological analysis shows a cyclic reccurance of the elements utilization in 5 years perriods

Such information may be used and for the environmental protection aims.

Key words: phytomass, heavy metals, biological utilization, accumulation, acauntment (content)

ИЗВОД

Љубенова, М. (1997).. Утилизација и акумулација на Zn и Mn во фитомасата на Quercus frainetto во различни региони во Бугарија. Екол. Зашт. Живот. Сред., Том 5, Бр. 1. Скопје.

Беше проучувана содржината на Zn и Mn во моделни дрвја од *Quercus frainetto* - дабот плоскач. Истражувањето беше направено со метод на атомска апсорпција во три различни фракции на фитомасата: листови, едногодишни гранчиња и дрвесина. Моделните дрвја беа избрани од три различни делови од земјата: Камчија Планина, Срнена гора и североисточните делови на Родопите. Беа направени дендролошки анализи на содржината.

Целта на ова истражување беше да се проучи биолошката кумулација, утилизацијата и корелативната зависност помеѓу содржината на овие витални микроелементи. Како резултат на анализите беа добиени некои интересни правилности. Беше најдено дека Zn се акумулира главно во дрвесината, а Mn во едногодишните гранчиња и листовите, што е поврзано со содржината на овие елементи во почвата.Се

установи правопропорционална зависност за Zn и обратна за Mn, помеѓу просечната содржина на елементите во испитуваната фракција во фитомасата и возраста на шумата. Дендролошките анализи покажуваат циклично повторување од утилизацијата на елементите на петгодишни елементи.

Ваквите информации можат да бидат искористени за целите на заштитата на животната средина исто така.

Клучни зборови: фитомаса, тешки метали, биолошка утилизација, акумулација, содржина

OBJECT AND METHODS

The researches consern *Quercus frainetto* Ten. model trees appointed after separating the tree layers in 3 different phytocoenoses:

1. Seminal forest of I-st bonitation; average age 125 years; canopy 0.7; fullness 0.8; d-25 cm; h-25 m and density 446 trees per ha, situated in the region of Kamchia mountain (the village of Staro Oriachovo, Varna destrier) on 150 m above the sea-level and west-northwest exposure.

This site is in the climatic region of the North Black Sea. The average annual amount of rainfalls is 578 mm and the average annual air temperature is 11.3 C. In this region has been observed a considerable period of drought (m.VI, X). The soils are Plano sols with pH from 3.7 to 5.8.

2. Low-stemmed offshoot forest from II bonitation; average 43 years; canopy 0.6-0.7; fullness 0.9; d-14 cm; h-15 m and density 667 trees per ha (82.28% of all trees are *Q frainetto* Ten.) situated in the region of Sarnena gora (the village Domlian, Karlovo district) on 400 m above the sea level, on the low part of a hill with slope 12 and eastern exposure. The site is in the Bechinde Balcan lowmountain climatic region The average annual rainfalls is 6.53 mm and the average annual air temperature is 11.5 C The period of drought is in m. VIII and m. X. The soils are Hromic luvisols with pH from 4.7 to 4.9.

3. Low-stemmed offshoot forest from III bonitation; average age 57 years; canopy 0.8-0.9; fullness 0.9; d-14 cm; h-15 m; density 820 trees per ha (96.58% of all trees are *Q. frainetto* Ten.), situated in the north-east parts of Rodopa mountain (the village of Virbovo, Charmanli district), on 300 m above the sea level, on the upper part of a hill with slope 6 and north-west exposure. The site is in the Dolnomarishko-Dolnotundjanski climatic region. The average annual rainfalls is 576 mm and the average annual air temperature is 12.9 C (Тишков 1982) „ In the region has been observed a long period of drought (m. VI, IX) and guite drought (m. V, X) , which means that the abode is with the most xerophytic character. The soils are Hromic luvisols (Пенков 1992).

The acauntment of Zn and Mn has been researched in 3 fractions of phytomass (wood, leaves and annual branches) of middle model trees, chosen after separating the tree layer in experimental plots (1-0.5 ha; 2-0.27 ha and 3-0.2.5 ha) of studied forests (Молчанов 1967; Родин 1967).

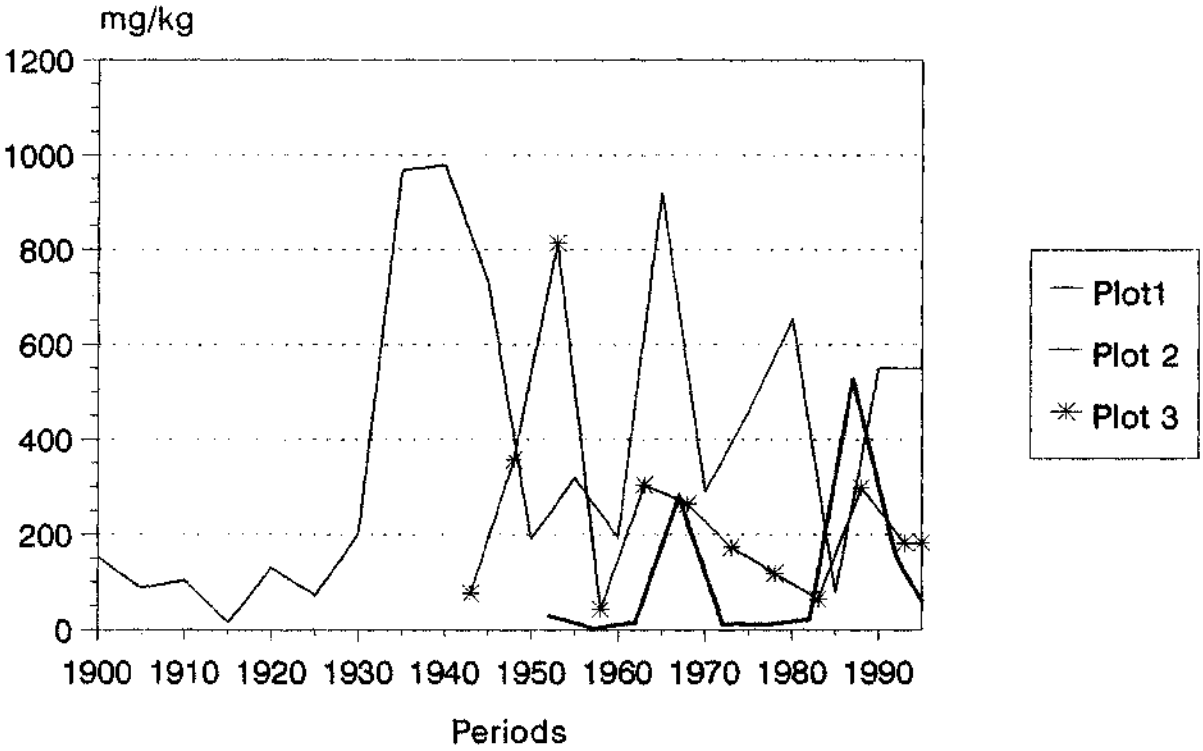
The samples of wood are taken with preslerov sfredei on 1.3 m night and western exposure. The elements are quantified dendrochronologicaly in 5 years periods (Iliev 1980). The average leaves samples and these of annual branches are taken after cutting down the trees (IX, 1995 year), dried to absolutely dry condition and powdered in appropriate way.

The acauntment of Zn and Mn is researched also in the different soil horisonts in dried to air-dry condition and powdered samples taken from the experimental sections, after cleaning them from biomass and shingles.

The analytical quantifying of Zn and Mn in the samples is made by AAC PERKINELMER 3030 spectrofotometer by useing the method of wet mineralization of vegetal and soil samples on BDS. The parameters of RAEOP (Relative acauntment of the element in the organs of the plant) and Ax (coefficient of biological utilization) are calculated. For a model organ is chosen the wood and for Ax is taken the average acauntment of the elements in the soil or in its different horizonts (Перелх>ман 197.5). The results are worked statistically (Генчев 1975).

RESULTS AND DISCUSSION

The quantified average acauntment of Zn in the wood of the researched models from the 3 regions is 245.733 $mg \cdot kg^{-1}$. In the sample from region 1 is found the highest acauntment of Zn (373.782+161.536 $mg \cdot kg^{-1}$) on the second place is the sample from region 3 (245.579+783 $mg \cdot kg^{-1}$) and the one from region 2 the lowest acauntment of Zn (117.839+135.290 $mg \cdot kg^{-1}$). As it is known that the researched trees are from different age classes (respect. 12; 6 and 4 for models 1.3 and 2), the dependence between age and average acauntment of Zn may be defined. The average acauntment is increasing in the older trees. The higher acauntment of Zn in plot 1 (12.4 times to the published results from Лгобенова 1993 for *Q. frainetto* Ten and 106 times from the results for other species from *p.Qitercus* Братанова 1988) may be connected with the higher acidity of the soil, so that the mobility of the heavy metals and their utilization by the vegetals are increasing (Малинова 1988; Христова 1989). The comparative analysis of the dynamics of accumulation of Zn in the wood of *Q. frainetto* Ten. from the 3 researched regions (Fig.1) shows big changes of the acauntment in five years periods, which causes the large intervals of the average results that show irregular utilization and the min and max of the accumulation. The cyclic recurrence of the maximums is possibly connected with cyclic changes of the climat, provoked by the peculiarities of the nature in the region (soil, human influence, etc.). In the older forest is possible, because of the higher number of maximums, to increase the whole average concentration of Zn in the wood. The period in which are reached the highest results in the acauntment of the element and in the 3 plots is 1965-1972 years. For instance, one of the highest results (919.960 $mg \cdot kg^{-1}$) for 125 years is noted in the period 1965-70 y. for model 1, for model 2 (280,037 $mg \cdot kg^{-1}$) in 1967-72 y and for model 3 (264 $mg \cdot kg^{-1}$) in 1968-73 y. This fact is possibly connected with increasing biological utilization of the element in this periods, connected with changes in the wetting and (or) with the industry. In models 2 and 3 is observed an active accumulation of Zn in period 1988-92 y. as well (model 1 -572.597 $mg \cdot kg^{-1}$; model 2 - 299,094 $mg \cdot kg^{-1}$), after which comes a clear tendency of decrease of its acauntment. After 1992 y. in our country most of the industrial factories stopped work.



Fig, l Dynamics of Zn accumulation in the wood of *Quercus frainetto* models
Сл.. 1 Динамика на акумулацијата на Zn во дрвесина од моделни стебла од *Quercus frainetto*

The average acauntment of Zn in the leaves of the models is 55.542+0.912 mg·kg^{-1}. The results put the models in order: 2; 1; 3 (78,577mg·kg^{-1} for 1; 59.599 mg·kg^{-1} for 2 and 28.450 mg·kg^{-1} for 3). This shows that the highest acauntment of Zn is in the leaves of the 45 years-old model from Sarnena gora, in which the acauntment in the wood is the lowest.

The average acauntment of Zn in annual branches of the researched models is 82.022+1.097 mg·kg^{-1}. The results put the models in order 3; 1 and 2 respecting·kg^{-1}: 113.906; 101.593; and 30.566, The highest acauntment of Zn is in the 57 years - old model from North-East Rodopy.

The results for Zn are high in the all 3 fractions in plot 1, which is on first place for the wood and on second- for the other fractions. This is connected with the higher pH of the soil.

The results for the acauntment of Zn in the researched fractions put them in the next order:

wood > annual branches > leaves.

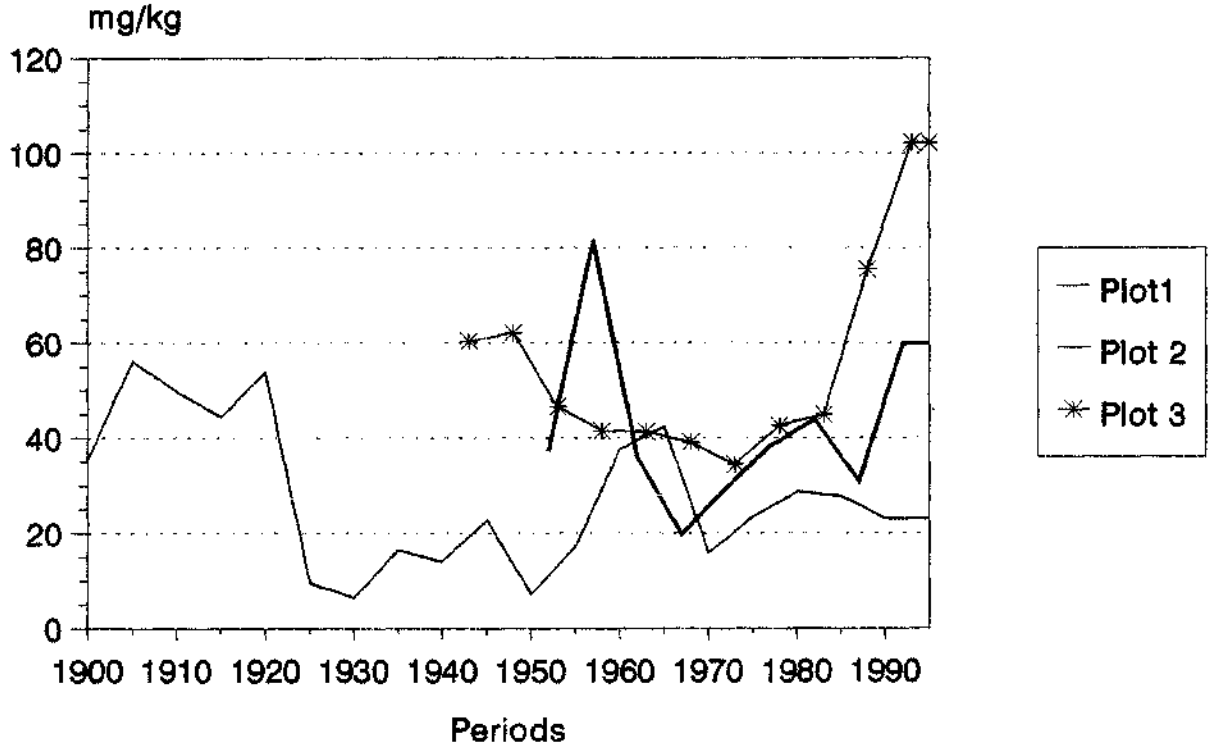


Fig. 2 Dynamics of Mn accumulation in the wood *Quercus frainetto* Ten. models Fig. 2 Динамика на акумулацијата на Mn во дрвесина на моделни стебла од *Quercus frainetto* Ten.

The leaves (RAEOP-0 22) and the annual branches (RAEOP-0.3) are in the group of the moderate deconcentrators of Zn. The average acauntment of Mn in the wood of the researched models from 3 regions is 41.216 mg·kg^{-1}. The highest results are in model 3 (53.701+13.389 mg·kg^{-1}) followed by those of model 2 and 1 (resp.mg·kg^{-1}: 41.920+13.962 and 28.026+7.555) This shows that, unlike Zn, the average acauntment is highest in the 43 years-old model and lowest in the 125 years-old one. The researchment of the dynamics of accumulation of Mn in the wood of *Q. frainetto* Ten. from 3 regions (Fig.2) shows big changes of the acauntment in 5 years periods. There are large intervals of the results and cyclic (min and max) utilization. The analysis of the graphical dependences shows that in plot 3 for the period 1953-88 y. observed only slight canges. The biggest diffrencies in the results are for model 1. For the period 1970-75 y. in the 3 plots is observed low acauntment of Mn in the wood. The registrated minimums for model 2 and 3 are in this period. The same results for models 2 and 3 are observed in the period 1962-95 y., which is possibly connected with the same soils and character of forists (offshoot one).

The average acauntment of Mn in the leaves fraction of the models is 354.324+0.348 mg·kg^{-1}. The results put them in the next order:

2; 3; 1 (resp. $mg \cdot kg^{-1}$: 414,933; 356,354; 291.686) , which shows that the highest results are in the 45 years-old model,

The average acauntment of Mn in annual branches is 472.917+0.746 $mg \cdot kg^{-1}$ (resp. $mg \cdot kg^{-1}$ for 1; 2 and 3 models: 675.722; 387.837 and 355.193), which shows that the highest results are in the 57 years-old model.

The average acauntment of Mn in the leaves and in the annual branches is 6.4 and 5.8 times higher than acauntment of Zn in these fractions.

The acauntment of Mn puts the fractions in the next order:

Annual branches > leaves > wood.

The annual branches (RAEOP^{-1} l,05) and the leaves (RAEOP-8, 6) During the research-ment of the acauntment of Zn and Mn in the soil profiles from 3 plots (Tab.l) is observed a tendency of increase for the results of Zn in depth, which confirens the published results for high acauntment of Zn in the low C horizont of the different kinds of soils (Фаитонджиев 1982),

This research confirms that the wood of *Q. frainetto* Ten. is accumulator of Zn and causes Zn exhanstion in the soil.

The highest results for Mn are registrated in the upper humus levels, which is possibly connected with the accumulation of the element in the annual branches and in the leaves. This element returns in this horizonts after mineralization of the litter-fall.

Tab. 1 Contents of Zn and Mn ($mg \cdot kg^{-1}$) in the soils of the investigated plots
Таб. 1 Содржина на Zn и Mn ($mg \cdot kg^{-1}$) во почвите од истражуваните плотови

	soil layers (cm) почвени слоеви	Zn	Mn	pH
PLOT 1				
A11	0-20	31.340	105.192	4.5
A11Ag	20-39	31.895	94.620	4.2
B1tg	39-61	29.295	75.202	3.8
B2tg	61-84	27.087	97.416	3.7
BCk	83-125	38.783	206.373	5.8
PLOT 2				
AhA1	0-6	20.453	87.270	4.8
A2	6-18	18.305	88.993	4.7
B1	18-30	34.124	93.991	4.7
Bst	30-41	53.496	77.439	4.9
BC	41-62	40.855	76.972	4.9
PLOT 3				
Ah	0-9	35.998	111.188	4.8
AB	9-23	35.099	89.388	4.7
B	23-43	46.310	58.113	4.7
BC	43-65	35.074	124.318	4.9

The average Ax for Zn is 4.55; for Mn it is 3.28, which shows that *Q frainetto* Ten. is a strong utilizator of this elements (Tab. 2). The results for[1] Ax put the plots in the next order:

Zn - 1 > 2 > 3 ; Mn - 3 > 2 > 1 .

The highest utilization of Zn is in plot 1 and this of Mn is in plot 3.

The results for Ax in the different fractions of phytomass build the next order':

Zn : Ax wood > Ax annual branches > Ax leaves;

Mn : Ax annual branches > Ax leaves > Ax wood.

As it was already noted, all the researched fractions of phytomass are biological accumulators of Zn and Mn, expt the wood, which does not accumulate Mn - Ax=0.7.

Tab. 2 Coefficient of biological absorption (Ax) of Zn and Mn of the investigated *Q.frainetto* Ten, models

Tab. 2 Коефициент на биолошка апсорпција (Ax) на Zn и Mn од истражуваните моделни стебла на *Q. frainetto* Ten.

fractions (фракции) / plots (плотови)	annual leaves овогодишни листови	branches гранки	wood дрвесина	average просечно
Zn	1 81	2.45	9.40	4.55
1.	1 91+0.28	3.25+0.53	17.86+0.83	7.67
2.	2.76+1.41	1.08+0.54	5.48+2 80	3.11
3.	0.76+0.14	3.03+0.53	4.86+0.83	2.88
Mn	3.93	5.22	0.7	3.28
1.	2.28+1.03	3.76+1.36	0.22+0.08	2.27
2.	4.91+0.50	4.21+0.44	0.71+0.08	3.28
3.	4.05+2.42	7.68+3.86	1.16+0.58	4.30

Note: Confidential intervals show the variation of Ax in soil horizons.

Забелешка: Интервалите на доверливост покажуваат варијација на Ах во почвените хоризонти

CONCLUSIONS

1. The average acauntment of Zn in the wood of studied models is 45,733 mg kg''' and it is higher than the published by Лгобенова (1993) and Братанова (1988) results.

2. In the older forists the acauntment of Zn in the wood is increasing, because of existing cyclic recurrence in its utilization, and because of the biggest number of maximums, and preferencial utilization of the elements in the wood.

3. The average acauntment of Zn in the leaves fraction is 55,542 $mg \cdot kg^{-1}$; in the annual branches fraction - 8.022. It is two times lower than published results for *Q cerris* L, and two times higher than those for *Q. robw* L, (Гатева 1994; Братанова 1988).

4. The leaves and the annual branches are moderate deconcentrators of Zn (RAEOP - 0.22 to 0,33).

5. The results for Zn are high in the all 3 fractions in plot 1, which connected with the lower pH of the soil in the region, higher volatility and ability of utilization of the element.

6. The dynamics of accumulation of Zn is connected with the cyclic unsteady utilization, and the big number of min and max, connected with cyclic changes, caused by regional peculiarities of the nature (climat, soil, human influence, etc).

7. There was not found a lack of differences between min and max of accumulation of Zn in studied plots, because of the different origin and age of the trees, and also because of some regional peculiarities.

8. High results for the acauntment of Zn in all studied plots are observed in the period 1965-1975 y,,, for plots 1 and 2 1988-1992 y also.

9. In the last 3 years is observed of decrease of the acauntment of Zn in the wood, which is probably connected with the causes of the industry in our country.

10. The average acauntment of Mn in the wood of the studied models from the 3 regions is 41,216 $mg \cdot kg^{-1}$, which is close to the published results for *Q robw* L. (Братанова 1988) and is at about 6 times lower than the acauntment of Zn in this fraction. acauntment of Mn in the wood is in a direct ratio to the age of the forest, because of the accumulation of the element manly in the annual branches and leaves.

11. The average acauntment of Mn in the leaves fraction is 354.324 $mg \cdot kg^{-1}$; in the annual branches - 472.917 $mg \cdot kg^{-1}$ and is 6.4 times (for leaves) and 5,8 times (for annual branches) higher than the acauntment of Zn in these fractions. The result for leaves fraction is 3 times lower than those published for *Q, pubescens* Willd. and 1.7 times lower than those for *Q. roburL.* (Гатева 1994; Братанова 1988)

13. The leaves and annual branches are moderate concentrators of Mn (RAEOP 11.5 and 8.6).

14. The results for Mn are high for' all studied fractions in plot 3, which is possibly-connected with some geological peculiarities of the region.

15. The accumulation of Mn in the wood is cyclic too. In plot 3 are observed only slight differences; in plot 1 are redistricted the highest variation of results.

16 In the all 3 regions is observed low accumulation of Mn for the period 1970-1975 y. For plots 2 and 3 such a period is also 1962-1995 y., which is possibly connected with the equal kind of soil there

17. The acauntment of Zn and Mn in the soil of the regions is lower than the average one of the country (Мирчев 1971).

18. There is a tendency of increase of the acauntment of Zn and decrease of this of Mn in depth, because this ligueoms sort causes exhanstion of Zn in the soil, accumulating it in the wood, and concentration of Mn in the upper humus horizonts, accumulating it in the leaves and annual branches.

19. *Quercus frainetto* Ten. is a strong accumulator of this trace elements (Ax: 4,55 for Zn and 3.28 for Mn).

20. All the researched fractions of phytomass are accumulators of Zn and Mn, except the wood, which is accumulator of Zn but not of Mn.

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УТИЛИЗАЦИЈА И АКУМУЛАЦИЈА НА Zn И Mn ВО ФИТОМАСАТА НА QUERCUS FRAINETTO ВО РАЗЛИЧНИ РЕГИОНИ ВО БУГАРИЈА

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РЕЗИМЕ

Во трудот е прикажана истражувањето на содржината на Zn и Mn во избрани модеини дрвја од *Quercus frainetto* Ten. Истражувањето беше направено со метод на атомска апсорпција во при различни фракции на фитомасата: листови, едногодишни гранчиња и дрвесина. Моделните дрвја беа избрани од при различни делови од земјата: Камчија Планина, Срнена Гора и североисточните делови на Родопите. Беа направени дендролошки анализи на таа содржина..

Цел на истражувањата е да се направи ревизија на постоечката литература за биолошката акумулација и корелативната зависност помеѓу содржината н овие витални микроелементи Во текот на истражувањето се добиени интересни законитости.

1. Цинкот се акумулира првенствено во дрвесина;га, а листовите и едногодишните изданоци умерено го користат (RAEOP – 0.22 и 0.33), додека манганот умерено се концентрира во листовите и едногодишните изданоци (RAEOP - 11.5 и 8.6) Од сите истражувани фракции само дрвесината не е биоакумулатор на манган (A-0.7).

2. Се набљудува правопропорционално по однесувањето на цинкот и обратнопропорционално по однесувањето на манганот зависноста помеѓу средната содржина на елементите во истражуваните фракции фитомаса и возраста на шумата.

3.. Добиените вредности за цинкот кај сите фракции се повисоки во плот 1 (поради повисоката pH на почвата, а за манган во плот3 (поради геолошките карактеристики

4. Дендролошката анализа покажува добра изразена, особено кај цинкот, цикличност во кружењето на елементите при петгодишни истражувања, која се должи на климатските флуктуации под влијание на регионалните особености (клима, почва, антропоген фактор.

5 Не е утврдено апсолутно совпаѓање на миниумот и максимумот во натрупувањето на елементите во трите плота поради разликите на регионалната клима, почвата, производството и возраста на дрвјата.

6. Содржината на елементите во почвата на истражуваните региони е пониска од средините вредности за Бугарија (Мирчев 1971). Се забележува зголемување на содржината на цинкот во длабочина на почвениот профил, додека најбогати со манган се горните хумусни слоеви Тоа е како резултат на фактот дека сите фракции на фитомасата на *Quercus frainetto* Ten. се биоакумулатори на цинк, особено дрвесината, што доведува до исцрпување на почвата со цинк За разлика од цинкот, манганот се на1рз'пз7ва во листовите (Ах - 3 9.3) и едногодишните изданоци (Ах - 5.22). Дрвесината не акумулира манган, шхо е во врска со зголемување на концентрацијата на манганот во горните хумусни слоеви на почвата.