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Distribution of Mineral Substances in Different Wood Tissues of European Larch (*Larix decidua* Mill.)

Raspodjela mineralnih tvari u različitim drvnim tkivima europskog ariša (*Larix decidua* Mill.)

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ABSTRACT • Typical wood tissues, such as stemwood, bark, branches, twigs and needles, of two very old European larch trees (*Larix decidua* Mill.) were examined for the content of macro and micro mineral substances. Elemental analysis, atomic absorption spectrophotometry (AAS) and ultraviolet/visible (UV/VIS) techniques were applied for quantitative determination of individual elements. The results indicated that both trees had almost identical mineral content. The highest contents of macro elements N, P, S, K and Mg as well as micro elements Ni, Fe, Al and Co were measured in needles, while Ca, Mn and Zn prevailed in bark. Concentrations of substances were the lowest in stemwood. Comparison with similar studies of foliar mineral distribution proved that both trees had good nutrient status, which corresponded to their condition.

Keywords: European larch, micro and macro nutrients, AAS, elemental analysis, foliar mineral distribution

SAŽETAK • U radu se prikazuju rezultati istraživanja sadržaja mikromineralnih i makromineralnih elemenata u tipičnom drvnom tkivu dvaju stabala vrlo starih europskih ariša (*Larix decidua* Mill.) kao što su stablo (deblo), kora, grane, grančice i iglice. Za kvantitativno određivanje pojedinačnih elemenata primijenjene su elementarne analize, atomska apsorpcijska spektrofotometrija (AAS) i ultraľubičasta/vidljiva (UV/VIS) analitička tehnika. Prema dobivenim rezultatima, svi su usporedivi uzorci oba drva imali praktički jednak mineralni sastav. Najveći sadržaj makroelemenata N, P, S, K i Mg, kao i mikroelemenata Ni, Fe, Al i Co, zastupljen je u iglicama, no Ca, Mn i Zn prevladavali su u kori. Najniže koncentracije mineralnih tvari izmjerene su u drvu stabla (debla). U usporedbi sa sličnim studijama raspodjele mineralnih tvari u iglicama, dokazano je da svi uzorci drva imaju primjeren sadržaj tih tvari, što odgovara njihovom zdravom stanju.

Ključne riječi: europski ariš (*Larix decidua* Mill.), sadržaj mikromineralnih i makromineralnih tvari, atomska apsorpcijska spektrofotometrija, elementarna analiza

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1 INTRODUCTION

1. UVOD

Trees and other plants receive their nutritional elements from air, water and soil. The most basic building elements are carbon (C), oxygen (O) and hydrogen (H). Their sources are air and water. They combine to form higher structures such as carbohydrates, which compose plant tissues. Besides, there are at least 14 other mineral elements that are needed for the growth.

Minerals play an important role in plant metabolism. They are components of organic structures, such as proteins and nucleic acids, which are essential constituents of living organisms. They are charge carriers and osmotic regulators and serve as promoters of numerous enzymatic reactions. Their participation in the division and differentiation of cells as well as photosynthesis is also significant. In short, tree growth is in many ways dependent on mineral uptake and distribution (Fengel and Wegener, 1989; Leyton, 1957).

Most minerals are delivered to the tree from forest soil through its root system; however some can be absorbed through leaves. Total mineral contents and concentrations of individual elements vary within and between tree species and are also strongly dependent on ecological factors, i.e. the site where a tree is growing (Bujas, 1998; Antonović *et al.*, 2007; Antonović *et al.*, 2010). Typically, mineral contents of needles, leaves, bark, branches, twigs and roots are higher than those of stemwood. Younger trees are likely to contain higher concentrations of nutrients than mature ones and hardwoods are richer in them than softwoods. In most cases alkali and alkali earth elements such as potassium (K), calcium (Ca) and magnesium (Mg) make up to 80 % of the total inorganic constitution of softwoods and hardwoods. Among them Ca predominates constituting often up to about 50 % of the total inorganics. A variety of other elements can also be detected in wood tissues, altogether about seventy, however only 17 have been identified so far as essential, meaning that plant needs them to complete its reproductive stage of life cycle. These are the above mentioned carbon (C), oxygen (O), hydrogen (H), potassium (K), calcium (Ca) and magnesium (Mg) as well as nitrogen (N), phosphorus (P), sulfur (S), iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo), nickel (Ni) and chlorine (Cl). N, P, K, Ca, Mg and S are considered major or macro-nutrients, because they are required in large quantities that range between 1 to 150 g per kg of plant dry matter. Fe, Zn, Mn, Cu, B, Mo, Cl and Ni are minor or micro-nutrients that are required in amounts from 0.1 to 100 mg per kg of dry matter (Henry *et al.*, 1992; Merilä and Derome, 2008; Ditmarova *et al.*, 2007).

There is also a distinctive difference between nutrient minerals according to their mobility. Mobile nutrients are those able to move out of older plant parts to younger ones when supplies are not adequate. Mobile elements are N, P, K, Cl, Mg and Mo. In contrast, immobile nutrients are B, Ca, Cu, Fe, Mn, Ni, S and Zn. Typically they cannot move quickly or not at all from

one plant part to another (Stenius, 1999; Raven *et al.*, 2005; Rowell, 2005).

The role of individual elements can be fairly well explained but not always fully. N is contained in all enzymes essential for plant functions, P is a component of ATP, a compound that supplies the energy to grow and maintain the plant, K activates certain enzymes and balances the charge between ions, S is a part of certain amino acids and all proteins, Ca is contained in cell walls, regulates cell wall construction and balances charge, Mg is the central element within the chlorophyll molecule, B is important for sugar transport within plants and plays a role in cell division, Mo is needed for the reduction of absorbed nitrates into ammonia prior to incorporation into amino acids, Fe is a component of many enzymes and light energy transferring compounds, Zn is essential for plant hormone balance, Mn is a cofactor in many plant reactions, Cu is a component of enzymes involved in photosynthesis while Cl is a charge balancing ion (Raven *et al.*, 2005).

Deficiency of individual macro and micro elements results in specific growth disturbances as well as overall plant health deterioration due to the fact that essential biochemical and physiological processes are interrupted. Proportions among elements should also be balanced in order for the plant to achieve optimal uptake of all the necessary minerals (Ericsson *et al.*, 1993; Katzensteiner *et al.*, 1992; Mandre and Kuznetsova, 2004; Cape *et al.*, 1990; Ingestad, 1979). Nutritional condition of a living tree can be typically evaluated by chemical analysis of needles or leaves, respectively. Less common is the evaluation based on stemwood minerals characterization (Ericsson and Rosen, 1994; Komlenovič *et al.*, 1995; Myre and Camiré, 1996)

Total inorganics in wood can be evaluated by determination of ash content after combustion of plant material. Woods typically contain from 0.1 to 1.5 % of ash, however in some tropical species these values may be exceeded. The ash is predominantly composed of different metal oxides, silicates, carbonates and other salts. Individual elements can be determined either from ash or after acidic digestion of plant material by various analytical techniques such as atomic absorption spectroscopy, colorimetry and elemental analyses (Stelzer *et al.*, 1993).

The aim of our research was to evaluate concentrations of different essential elements as well as cobalt and aluminum in various anatomical parts of two healthy and very old European larches in order to define variations within individual tree as well as between trees growing in the same area. The data will be useful for further studies of relations between mineral constitution, growing conditions and plant health.

2 MATERIAL AND METHODS

2. MATERIJAL I METODEDE

2.1 Samples

2.1. Uzorci

Two larch trees (*Larix decidua* Mill.) were felled at the end of June in the Alpine region of Slovenia at

the altitude of 1000 m. They were growing in a mixed forest among beech and spruce trees. Both were 180 years old and about 30 m high. They were healthy as they had good living conditions provided by rich forest soil (brown, carbonate ground).

5 cm thick discs were cut from the trunks at the base (20 cm above ground) as well as at the heights of 8, 18 and 28 m. A living branch was taken from each tree at the height of 18 m. A part, up to 1.5 m from the trunk was used for analyses. Twigs (about 0.5 cm wide) and needles from the same branch were also collected (about 500 g of each).

Discs as well as branches were debarked and cut into smaller pieces. Samples, including stemwood, branchwood, bark, twigs and needles, were frozen at -24 °C till analysis. Stemwood bark was treated as only one bulk sample, so it was not divided according to the height levels. Samples were vacuum dried at 30 °C, ground to wood meal and homogenized before combustion and digestion.

2.2 Analyses

2.2. Analyze

Ash content

All samples were analyzed for the content of ash (550 °C) according to the DIN EN 12879 standard method.

FTIR spectra

Spectra of ash samples were recorded on Biorad-Excalibur spectrophotometer as transmission spectra on KBr pellets in the range between 4000 and 400 cm⁻¹.

Elemental analyses

C, N and S were analyzed on CNS LECO 2000 instrument for elemental analysis, which was equipped with IR and thermoconductivity detectors.

Determination of phosphorus

P was determined spectrophotometrically after digestion of samples with conc. H₂SO₄ and HNO₃. Concentration of P was measured in diluted solution according to the ISO 6878 standard (ammonium molybdate method).

Determination of K, Ca, Mg, Cu, Ni, Co, Fe, Mn, Zn, and Al

Samples were digested by HNO₃ and H₂O₂. Concentrations of individual elements were measured by AAS technique on Varian SpectrAA 220 instrument using electrothermal atomization for Cu, Ni, Co, Al and flame ionization for K, Ca, Mg, Mn, Fe, Zn.

All analyses were performed in 3 parallels. The results are average values of individual measurements. They are expressed as % (w/w) for ash content and N, as g/kg for P, K, S, Mg and Ca and as mg/kg for Cu, Ni, Co, Fe, Mn, Zn and Al. All values are expressed per weight of dry sample.

3 RESULTS AND DISCUSSION

3. REZULTATI I RASPRAVA

Ash contents showed typical pattern of mineral distribution in the trees. Stemwood values increased

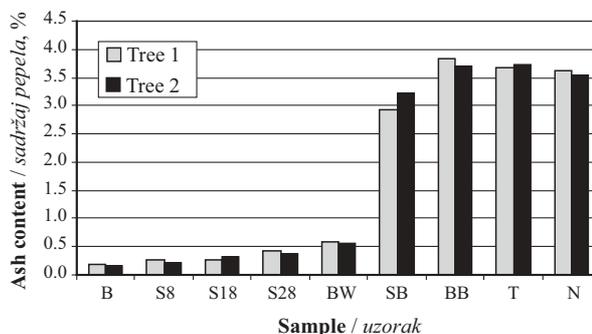


Figure 1 Ash content in larch samples of both trees

(B - stemwood at base (20 cm), S8 - stemwood at 8 m, S18 - stemwood at 18 m, S28 - stemwood at 28 m, BW - branch wood, SB - stemwood bark, BB - branch wood bark, T - twigs, N - needles)

Slika 1. Sadržaj pepela u uzorcima iz oba stabla ariša

(B - stablo u bazi, 20 cm, S8 - stablo na visini 8 m, S18 - stablo na visini 18 m, S28 - stablo na visini 28 m, BW - drvo grane, SB - kora stabla, BB - kora grane, T - sitne grane, N - iglice)

with increasing height of the trunks. Characteristic ash concentrations were between 0.15 and 0.43 % and there was little difference between both trees. Branch wood contained slightly more ash than the trunk parts. Typical values ranged from 0.5 to 0.6 %. In contrast to the wood samples, bark, twigs and needles contained much more inorganic material. They had similar ash concentrations, all of them approaching or exceeding 3 %.

The corresponding values are presented in Figure 1. FTIR spectra of wood and bark ashes showed practically no difference. There were intensive carbonate peaks with wave numbers of about 1440, 876 and 710 cm⁻¹. Silicate peak was also visible at 1050 cm⁻¹; however its intensity was poor. In contrast, twigs and needles gave spectra with much more abundant silicate peaks indicating that the concentrations of silicates increased from the trunk towards outer tree parts, such as bark, branches, twigs and needles.

FTIR spectra of ashes from stemwood, twigs and needles are presented in Figures 2, 3 and 4.

Distributions of N, P and S in different tree tissues showed similar pattern. Typically concentrations of N and P increased with tree heights, while the quantity of S remained more or less constant. Bark samples, twigs and needles proved to have relatively rich content of N and P, compared to the stemwood and branch wood. The highest average concentrations of all three elements were found in needles. They approached 2 % (w/w) for N, 3 g/kg for P and 1.7 g/kg for S, which is in good agreement with the results reported by Paques (1994) and Alriksson *et al.* (1998).

Distributions of N, P and S contents in different materials of both larch trees are presented in Figures 5, 6 and 7.

K and Mg exhibited practically the same concentration behavior as N and P, while Ca strongly predominated in bark samples, where the measured values ranged between 14 and 16 g/kg. The contents of Ca, Mg and K in needles were close to 8; 1.5 and 3 g/kg, which partly corresponded to the results published by

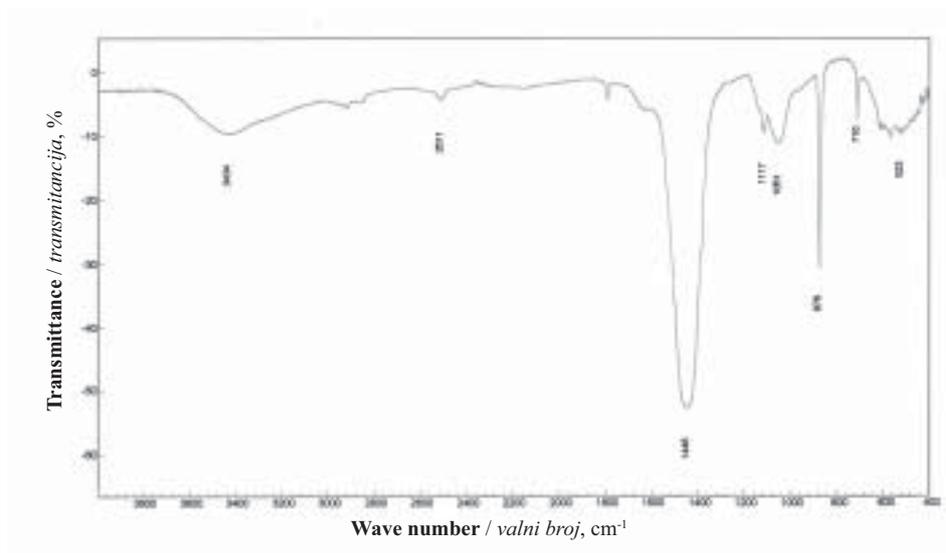


Figure 2 FTIR spectra of stemwood ash
Slika 2. FTIR spektar pepela od stabla

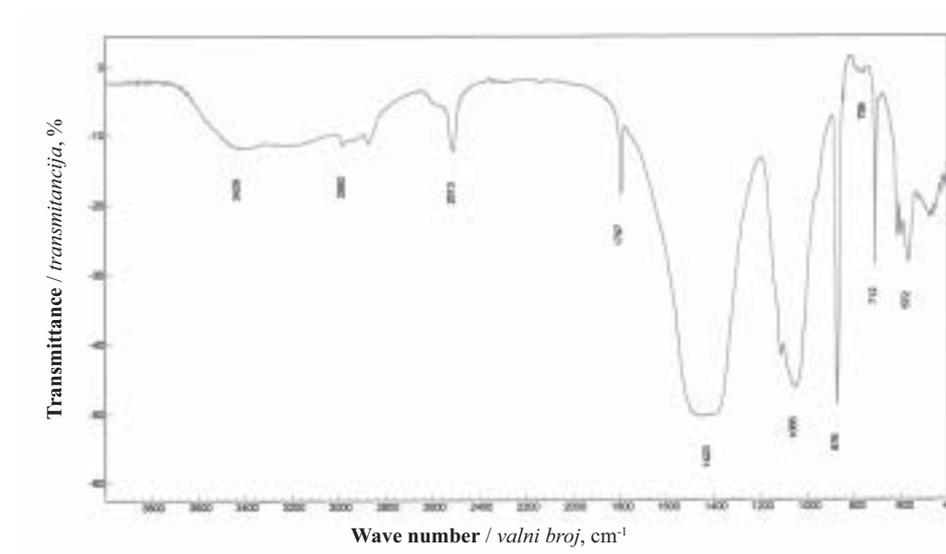


Figure 3 FTIR spectra of ash from twigs
Slika 3. FTIR spektar pepela od sitnih grana

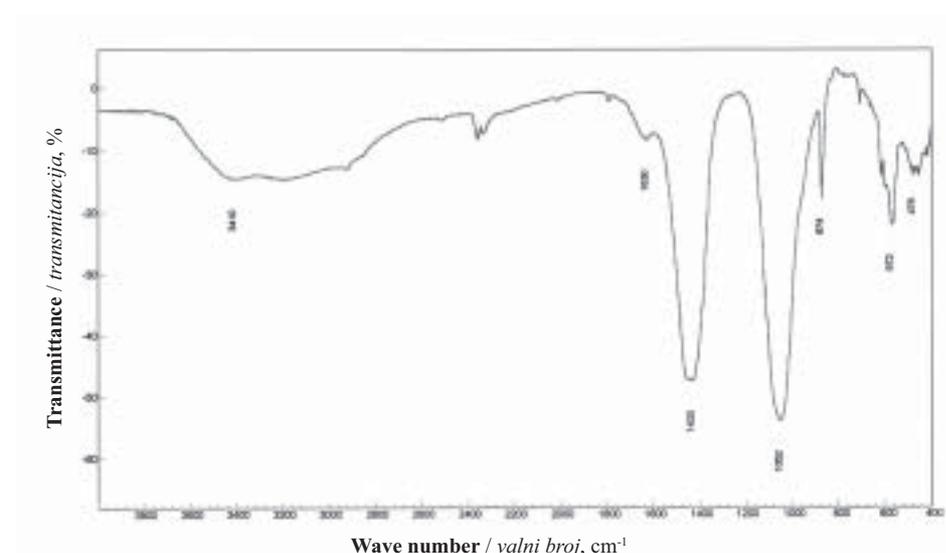


Figure 4 FT-IR spectra of ash from needles
Slika 4. FT-IR spektar pepela od iglica

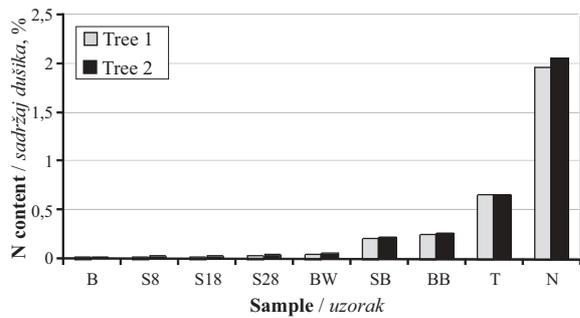


Figure 5 Nitrogen (N) content of larch wood tissues
Slika 5. Sadržaj dušika (N) u drvnim tkivima ariša

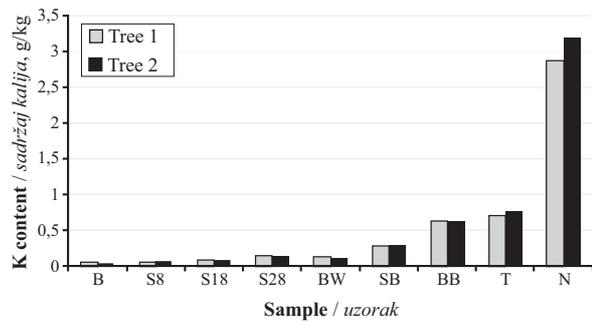


Figure 8 Potassium (K) content of larch wood tissues
Slika 8. Sadržaj kalija (K) u drvnim tkivima ariša

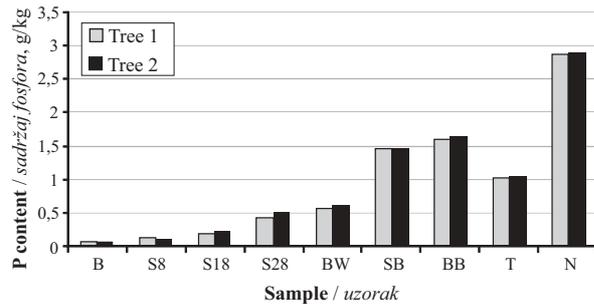


Figure 6 Phosphorus (P) content of larch wood tissues
Slika 6. Sadržaj fosfora (P) u drvnim tkivima ariša

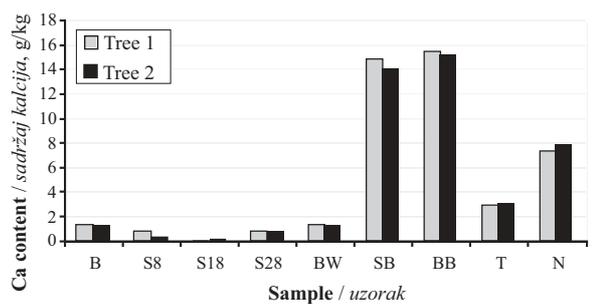


Figure 9 Calcium (Ca) content of larch wood tissues
Slika 9. Sadržaj kalcija (Ca) u drvnim tkivima ariša

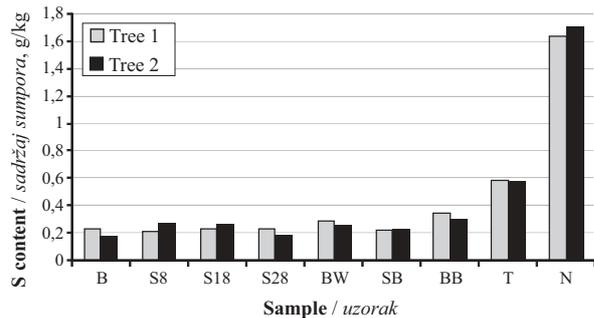


Figure 7 Sulphur (S) content of larch wood tissues
Slika 7. Sadržaj sumpora (S) u drvnim tkivima ariša

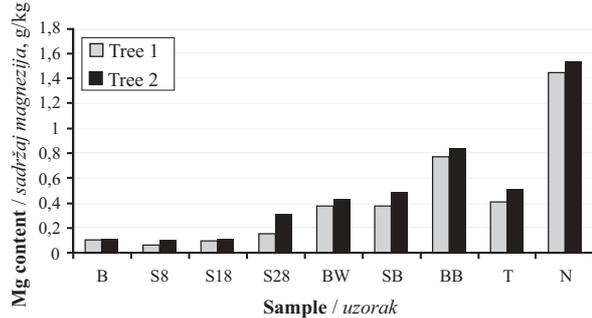


Figure 10 Magnesium (Mg) content of larch wood tissues
Slika 10. Sadržaj magnezija (Mg) u drvnim tkivima ariša

Paques (1994), Myre *et al.* (1996) and Alriksson *et al.* (1998), where the presented foliar concentrations of Ca and Mg in different larch species were similar, but those of K were typically somewhat higher.

According to our results, there was no significant difference between the two analyzed larch trees as far as the distributions of the six macro elements in various tree tissues are concerned.

K, Ca and Mg contents are shown in Figures 8, 9 and 10.

Distribution patterns of measured microelements Ni, Zn, Mn, Fe, Cu, Al and Co within different anatomical parts of both larch trees were highly variable. Some similarity was observed in case of Zn and Mn, as both elements prevailed in bark samples where their concentrations amounted to about 45 and 270 mg/kg, while needles contained surprisingly lower quantities and namely about 25 mg/kg of Zn and between 25 and 50 mg/kg of Mn. The concentrations of Mn were substantially lower, compared to the results of a similar study published by Myre *et al.* while values for Zn were quite comparable. The distribution of Zn and Mn

concentrations in different larch tissues are presented in Figures 11 and 12.

Ni, Fe, Al and Co predominated in needles where average concentrations amounted to about 1; 135; 200 and 0.6 mg/kg. Surprisingly high contents of Ni, Cu and Fe were determined in stemwood base samples (about 0.6; 12.5 and 30 mg/kg), which was not the case with other elements. Significant is also the fact that the lowest overall concentrations were measured for Ni, Cu and Co.

The results for Cu and Fe are in good agreement with the values obtained by Bending and Moffat (1999) in their systematic studies of foliar nutrients in Japanese larch. Average values of Ni, Fe, Cu, Al and Co analyses of larch wood tissues are presented in Figures 13 to 17.

It has to be emphasized that the repeatability of all macro and micro element determinations was very high due to efficient homogenization of samples before the analyses. Parallel measurements never differed more than 11 % from each other, even in case of low concentration elements, such as Co, Cu and Ni. The

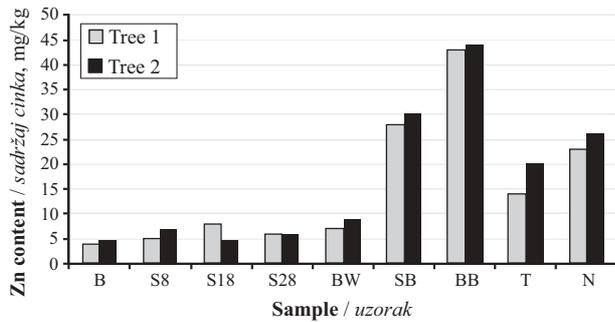


Figure 11 Zinc (Zn) content of larch wood tissues
Slika 11. Sadržaj cinka (Zn) u drvnim tkivima ariša

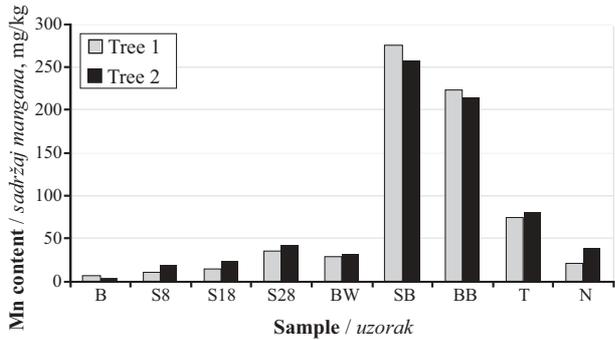


Figure 12 Manganese (Mn) content of larch wood tissues
Slika 12. Sadržaj mangana (Mn) u drvnim tkivima ariša

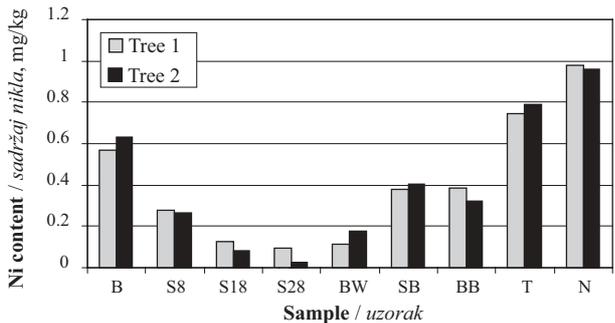


Figure 13 Nickel (Ni) content of larch wood tissues
Slika 13. Sadržaj nikla (Ni) u drvnim tkivima ariša

results indicated that the two examined larch trees exhibited surprisingly high similarity in their mineral structure and showed no pronounced deficiency in the content of most analyzed elements, which corresponded to their healthy condition.

4 CONCLUSIONS 4. ZAKLJUČCI

By determination of macro and micro nutrients in different larch tissues, a typical distribution pattern was obtained for each element. Most elements such as N, P, S, K, Mg, Ni, Fe, Al and Co predominated in needles, while Ca, Zn and Mn were most abundant in bark. External tree parts as for example bark, branches, twigs and needles had much higher inorganic contents than stemwood where the concentrations of individual elements increased with height.

According to FTIR spectra many elements in stemwood and bark were bound as carbonates in contrast to twigs and needles where silicates prevailed.

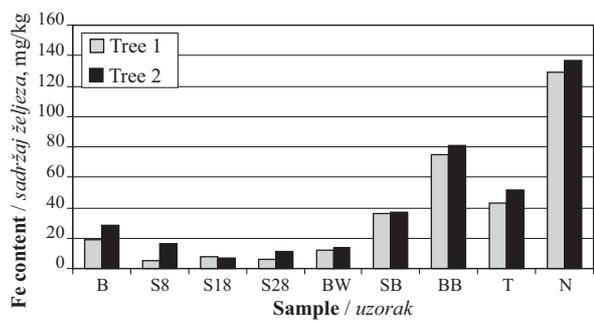


Figure 14 Iron (Fe) content of larch wood tissues
Slika 14. Sadržaj željeza (Fe) u drvnim tkivima ariša

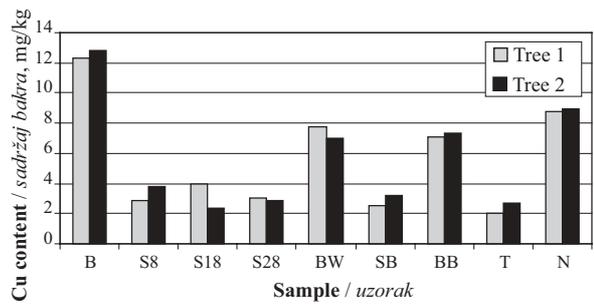


Figure 15 Copper (Cu) content of larch wood tissues
Slika 15. Sadržaj bakra (Cu) u drvnim tkivima ariša

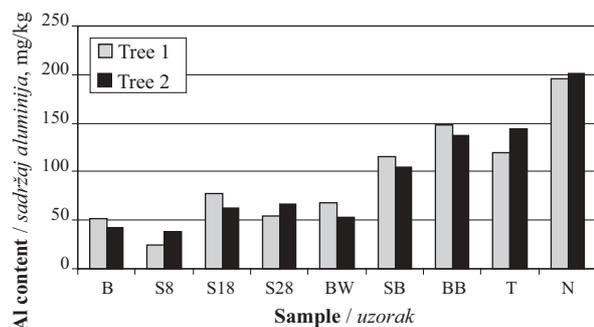


Figure 16 Aluminium (Al) content of larch wood tissues
Slika 16. Sadržaj aluminija (Al) u drvnim tkivima ariša

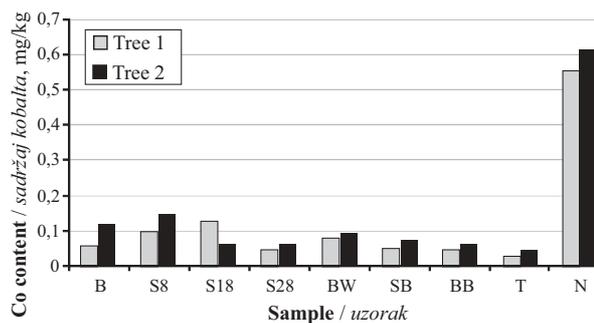


Figure 17 Cobalt (Co) content of larch wood tissues
Slika 17. Sadržaj kobalta (Co) u drvnim tkivima ariša

It was established by foliar analyses that nutrient status of both trees was good as most of the measured elements exhibited optimal or close to optimal values.

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