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INVESTIGATION AND EVALUATION OF COPPER AND ZINC CONCENTRATION TENDENCIES IN *Pinus sylvestris* L. TREE-RINGS

Pranas Baltrėnas[1], **Dovilė Vaitkutė**[2]

Department of Environmental Protection, Vilnius Gediminas Technical University, Saulėtekio al. 11, LT-10223 Vilnius, Lithuania
E-mails: [1]pbalt@vgtu.lt; [2]dovilev@vgtu.lt (corresponding author)

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Abstract. Free trace metals are one of the most relevant environmental problems of today; consequently, it is becoming important to evaluate their spatial distribution and accumulation rates in the natural environment. For this analysis, Scots pine (*Pinus sylvestris* L.) was chosen as suitable for indication of environmental stress because of its simple wood structure and of well distinct tree-rings for evaluation of temporal trace metals concentration changes. For the primary study, we chose the most evenly forested territory – the south-eastern part of Lithuania. The study results revealed that the background Zn concentration in Scots pines is 7.2 $mg \cdot kg^{-1}$ and that of Cu amounts to 2.5 $mg \cdot kg^{-1}$. The anomaly concentrations of both trace metals in Scots pine defined to be higher than 21.3 for Zn and 9.0 $mg \cdot kg^{-1}$ of d.w. for Cu. The Cu and Zn concentration in Scots pine stem distributed gradually with slightly increased values towards the bark. However, a lower concentration rate was noticed in the wood formed in 1930–1950, which agrees with the most extreme climatic period in Lithuania.

Keywords: zinc, copper, south-eastern Lithuania, Scots pine, tree-rings, background concentration.

1. Introduction

In environmental monitoring, trees are used as a good indicator of environmental change. As trees grow in the same environment for decades, they accumulate different elements during their lives. Some of these elements might be derived from anthropogenic activities. Thus, dendrochemical analysis – the chemical analysis of accurate dating of tree-rings – can be beneficial for the reconstruction of environmental pollution events (Padilla, Anderson 2002; Augustin *et al*. 2005; Stravinskienė, Erlickytė-Marčiukaitienė 2009).

Because of well distinct tree-rings, softwood species tree-rings that grow in a temperate climate zone have been successfully used for retrospective analysis of trace metals (TMs) near the pollution point sources (Watmough, Hutchinson 1999; 2002; Orlandi *et al.* 2002; Lageard *et al.* 2008; Kuang *et al.* 2007; Baltrėnaitė *et al.* 2010). Researchers also use dendrochemistry tools to track how acid rain affects soil chemical changes (Guyette, Cutter 1994; Berger *et al.* 2004; Martin *et al.* 2004; Augustin *et al.* 2005; Gauthier *et al.* 2007; Augustin 2009).

Consequently, in our study we have chosen a Scots pine (*Pinus sylvestris* L.) as the one of softwood species identified for ecological monitoring. Additionally, this species is suitably sensible for indication of environmental change related to anthropogenic activities (Stravinskienė 2002). Nowadays, only data regarding changes in pine needles have been successfully used for the monitoring of environmental quality near heavy industry enterprises in Lithuania (Kupčinskienė 2006). Also, pine bark was started to be used for the purpose of monitoring air pollution with TMs or sulfur/nitrogen oxides (Kaunelienė 2000). In Lithuania, investigation of Scots pine tree-rings was already used in the retrospective analysis of radionuclides (Pliopaitė Bataitienė 2010).

However, dating TMs pollution by using tree-rings is still complicated as metals can enter trees through different pathways (foliage, stem or roots). Scientists also have to deal with many obstacles in explaining how metals are stabilised in tree-rings and whether they really stable (Ruppert, Wischow 2006; Bukata, Kyser 2007)? Garbe-Schörberg *et al*. (1997) noticed the tendency that studies using softwood trees and tree sections for multiple year periods perform more successful research than the studies analysing deciduous trees and separate tree-rings.

Additionally, it is only possible to date precisely released TMs in the natural environment if there is no metal mobility between tree-rings; however, it is hardly probable. It is also claimed that the formation of heartwood in trees may cause transport of metabolic elements radially across the stem wood towards the pith (Martin 2003).

To the contrary, according to Garbe-Schörberg *et al.* (1997), there has been observed a significant difference in metal content between early wood and late wood. Metal concentrations were increasing towards the outer rings as younger tree-rings are narrower (smaller early wood amount) and affected by a greater environmental stress. For example, a negative correlation was found between Cu concentration in the tree-rings and tree-ring widths (Pantera *et al.* 2007). Butkus and Baltrėnaitė (2007) determined that concentrations of investigated trace metals were smaller and coincided with the period favourable for tree growth, namely from 1986 to 1995 (Stravinskienė 2002).

Despite all obstacles, chemical analysis of wood could be still beneficial for monitoring of environmental change as it is less expensive and less time consuming than building artificial monitoring stations or drilling deep wells for monitoring of groundwater quality. Now, samples of trees could be collected with the help of increment borers, which have already been successfully used in dendrochemical studies in Lithuania (Baltrėnaitė *et al.* 2010). Although, the wound still brings damage to a tree, it has an – ability to limit this damage in order to defend the remaining tissues from contamination (Norton 1998).

In our study, we are analysing Cu and Zn – two trace metals that are essential to trees and which are usually discussed in articles evaluating impact of smelters or thermal power plants on environment and human health (Larsson, Helmisaari 1998; Derome, Nieminen 1998; Pärn 2001; Schelle *et al.* 2008; MacDonald *et al.* 2011; Mihaljevič *et al.* 2011).

These two TMs differ in their behaviour in soil media and plant availability. During the study of Cu and Zn adsorption and interaction at different pH levels in a sandy soil (*Gleyic Podzol*), it was determined that adsorption of Cu and Zn increases with increasing pH. However, with the pH increase, Cu is adsorbed more intensively that Zn (Mesquita *et al.* 2002). This fact might be related to higher Zn bioavailability to trees in comparison with Cu. The biological accumulation coefficient for Zn is 19.60 and for Cu – 9.09 (Dobrovolskii 1998).

The most evenly forested region in Lithuania was chosen to determine the background Zn and Cu concentrations in Scots pine trees. In Lithuania, there are approximately 18 000 forests and only 9 big areas that cover over 20 000 ha of Lithuanian territory. As in time forests were eradicated from fertile soils for the benefit of agriculture, the biggest forest areas are found on low fertility soils, which are predominant in south-eastern part of Lithuania. For this reason and due to the ability to adapt well to poorly nutritious and acidic soils, pine trees are the predominant tree species in Lithuanian forests (~38%).

The current study was initiated to define (1) background and anomaly concentrations of Zn and Cu in Scots pine wood; (2) show their spatial distribution in south-eastern Lithuania; and (3) to determine the variations of baseline Zn and Cu concentrations in Scots pine tree-rings.

2. Object and method of research

2.1. The study site

The study site is located in south-eastern part of Lithuania (54° 44‘N; 25° 09‘E; 53° 54’S; 23° 18’W) (Fig. 1), in the eco-geographical region of Dzūkija and Sūduva Highlands. The eco-geographical region is divided in to four administrative counties: Lazdijai (with 18.73 people per km²), Druskininkai (with 53.33 people per km²), Varėna (with 12.62 people per km²) and Trakai (with 29.79 people per km²).

Lazdijai forest area occupies 34.9% (the biggest forest plot being the Kapčiamiestis Forest) of the total area. Varėna and Druskininkai counties are the most forested

Fig. 1. Study site location in Lithuania

with the forest cover exceeding 69.1% of the total area (the biggest forest – the Dainavos Forest). In Trakai County, the forested area covers more than 47.7% of the total area (the biggest forests are the Ropėja, Miškiniai, Rūdiškės and Rūdninkai forests).

The climate of the investigated territory is continental and is particular to the climatic region of south-eastern highlands, where the annual precipitation varies between 550 and 600 mm in the West and 600–700 mm in the eastern part of the territory. The period with snow cover usually lasts for 80–95 days.

The predominant soil in the investigated area is particular to the region of the Southeastern Plain where 87% of the soil is sand and sandy loam. The median Cu concentration in the soil varies from 5.6 to 6.8 mg·kg^{-1}, whereas the median Zn concentration ranges from 17.3 to 24.9 mg·kg^{-1} (Kadūnas *et al.* 1999).

2.2. Field Sampling

In order to define the distribution of concentrations across the south-eastern part of Lithuania, the sampling grid covering the biggest forest areas was designed of 10×10 km plots (Fig. 2). The tree sampling was performed in spring and summer of 2010.

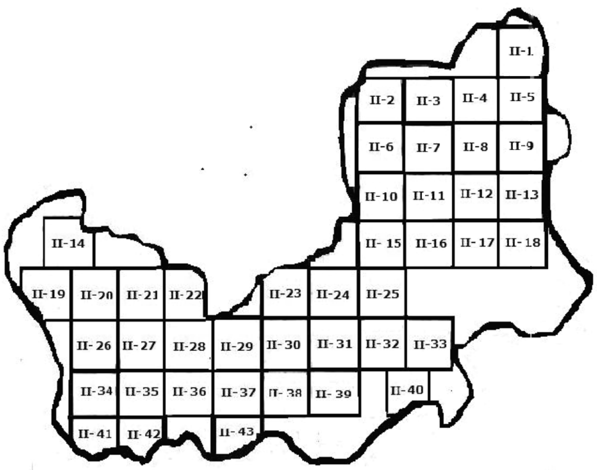


Fig. 2. Scots pine sampling grid for analysis of Cu and Zn, 10×10 km plots

One Scots pine tree was sampled in each plot. Tree core samples were taken from 1.3 m at the stem height in the north-south direction with a 12-mm-diameter Haglöf Presler borer. Healthy Scots pine trees with one stem and with more than 100 cm in circumference were chosen for the analysis.

In order to avoid anthropogenic distribution, all sampled trees were selected in a bigger than 0.5 ha forest areas and 200 m from the main roads and settlements (Bräker 2002).

For further analysis, tree cores were transported to the laboratory in paper straws. Tree cores were air dried and sanded. After tree-ring counting, each core was divided in to 20 ring sections (*n* = 165 sections). Each tree section was incinerated at 400 °C. The tree-ring counting was started from 2010 year ring.

In total, 42 trees were analysed of 77.88 ± 23.34 years in average age (Fig. 3). The oldest tree was 143 years old and the youngest was 36.

2.3. Elemental analysis

After ash mineralization in HNO_3:H_2O_2 (10ml:2ml; 65% and 37%) extraction solution for 31 min with ETHOS mineraliser (*Milestone*), elemental analyses in Scots pine wood and separate tree-ring sections, were performed by using *Buck Scientific 210 VGP* Atomic Absorption Spectrophotometer (FAAS).

2.4. Analysis of soil properties

Samples of the composite top soil mineral layer of 0–10 cm in thickness was taken under each Scots pine. Soil pH was measured by agitating air-dried soil in a mechanical shaker in a 0.01 M $CaCl_2$ solution, at 1:5 ratio for 1 hour, by using a calibrated digital pH meter (pH 538 WTV) (Fig. 4).

The total organic carbon content was analysed by dry combustion with total organic carbon analyser (TOC-V by SHIMADZU) at 900 °C (Fig. 5).

2.5. Statistical analysis

Each tree sample was measured in a duplicate (or replicated three times) and the mean values were used for further analyses. The basic statistical data analysis (a mean and a standard deviation) and mean comparison analysis were performed using the *Statistica* 7.0 and Statgraphics Centurion XVI programme tool package. The significance of differences between metal concentrations in the tree-ring sections was verified by using Student's *t*-test. Pearson correlation coefficients were calculated to evaluate the relationships between concentrations of metals in the tree wood and tree age or soil properties.

The background concentration is defined as the mean value of all measured data, i.e. C_b^i (whereas b – background concentration; i – number of samples), which distributes in the range of C_b^i ± 3*SD. The anomaly concentration of TMs is defined to be greater than C_b^i + 3*SD. For the detailed background concentration analysis, the anomaly concentrations were removed from the data list and the average, minimal and maximum concentrations were recalculated.

3. Results

3.1. Background concentrations of Cu and Zn in Scots pine and the spatial distribution

The average Zn concentration of all investigated Scots pines was equal to 7.22 ± 3.98 mg·kg^{-1} and the median Zn concentration was 6.55 mg·kg^{-1} (*n* = 165 d.w.). The minimum determined Zn concentration was identified at the 26th site and amounted to 2.05 ± 1.05 mg·kg^{-1}; meanwhile the maximum concentration was defined at the 36th site and amounted to 17.10 ± 4.20 mg·kg^{-1} (Fig. 6). However, none of the determined Zn concentrations were higher than the estimated anomaly concentration of 21.27 mg·kg^{-1}.

The average Cu concentration determined in Scots pines from south-eastern Lithuanian was equal to 2.52 ± 1.62 mg·kg^{-1} and the median value was 2.02 mg·kg^{-1} (n = 164 d.w.). The minimum Cu concentration was determined at the 13th sampling site and amounted to 0.42 ± 0.12 mg·kg^{-1}. The maximum of 7.02 ± 5.35 mg·kg^{-1} was determined at the 28th sampling site (Fig. 7). However, as in the case with Zn, these concentrations were not considered to be an anomaly as estimated anomaly concentrations in this region amount to 9.00 mg·kg^{-1}.

3.2. Trends of Zn and Cu in Scots pine tree-rings

3.2.1. Zinc trend in Scots pine tree-rings

Zinc concentration was distributed evenly in the separate tree-ring sections; the difference was statistically insignificant (ANOVA test, p>0.05) (Fig. 8). In the section of 20 tree-rings of the period 1980–2010, the Zn concentration distributed as follows: 7.72 ± 1.85 mg·kg^{-1} (n = 4 of d.w.);

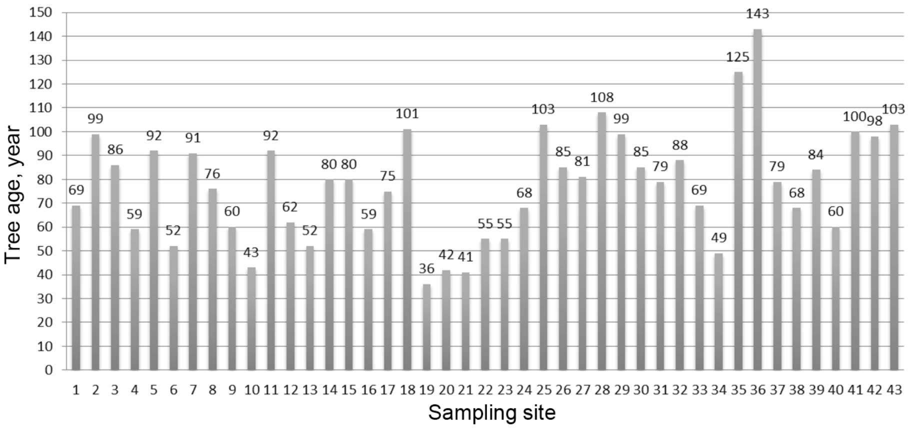


Fig. 3. Age of sampled Scots pine trees

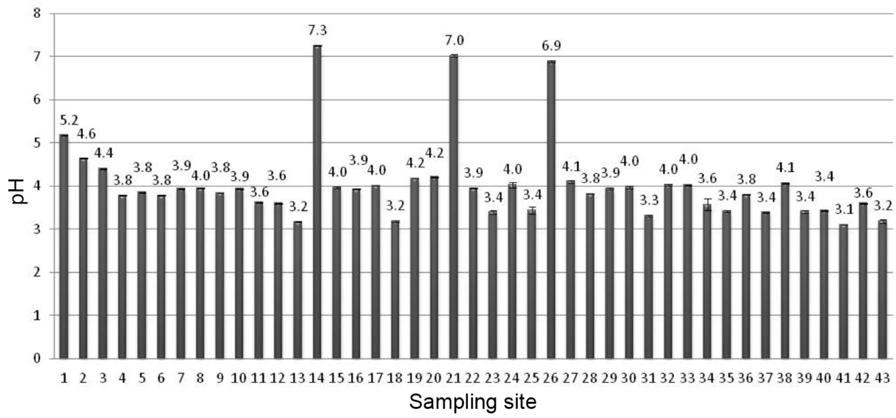


Fig. 4. Soil pH_{CaCl_2} in sampling sites. Bars represent the average value of measured duplicates ± SD

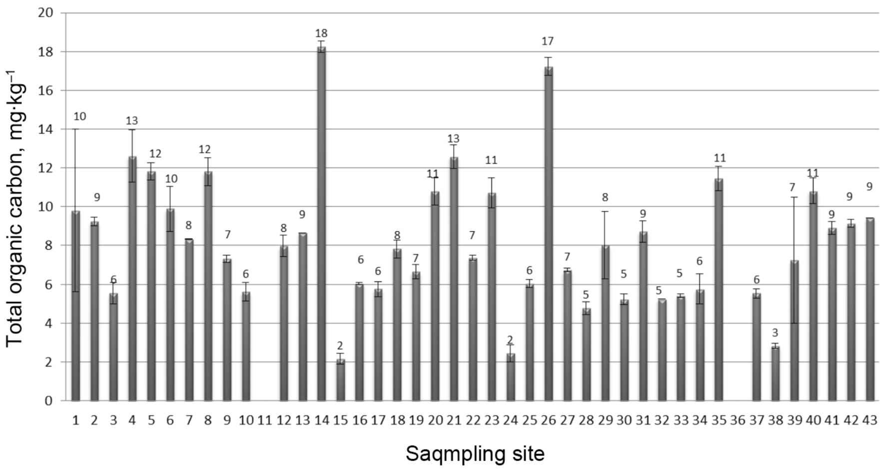


Fig. 5. Total organic carbon content in soil at sampling sites, mg·kg^{-1}. Bars represent the average value of measured duplicates ± SD

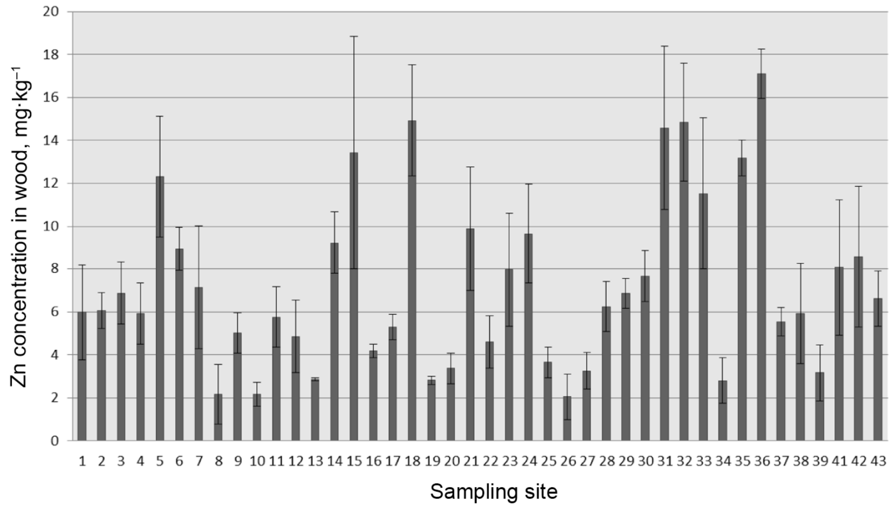


Fig. 6. Average zinc concentration in Scots pine wood at separate sampling sites (n = 42 d.w.). Bars represent the average value of tree-ring sections ± SD

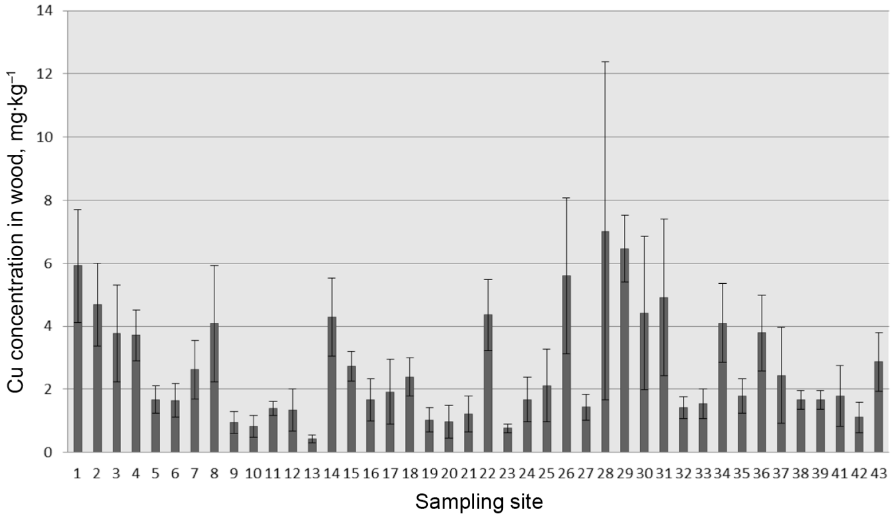


Fig. 7. Average copper concentration in Scots pine wood at separate sampling sites (n = 42). Bars represent the average value of tree-ring sections ± SD

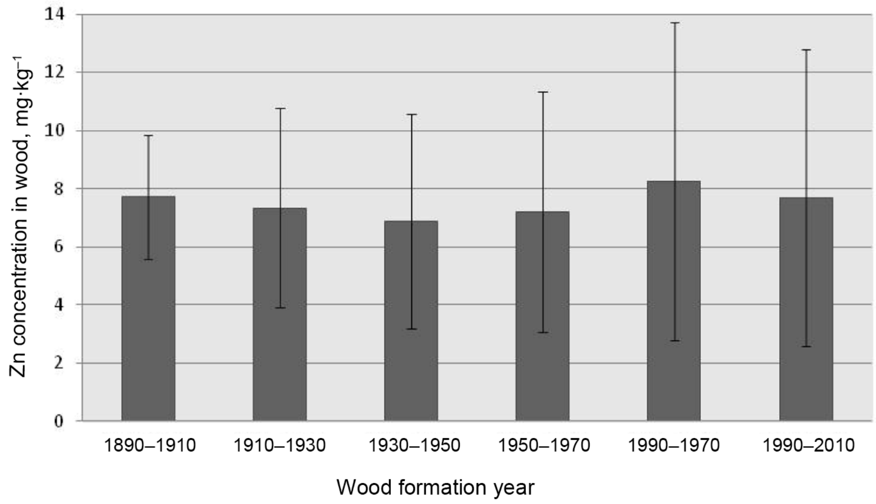


Fig. 8. Zinc concentration trend in Scots pine wood formed during 1910–2010 in south–eastern Lithuania. Bars represent the mean value ± SD of d.w.

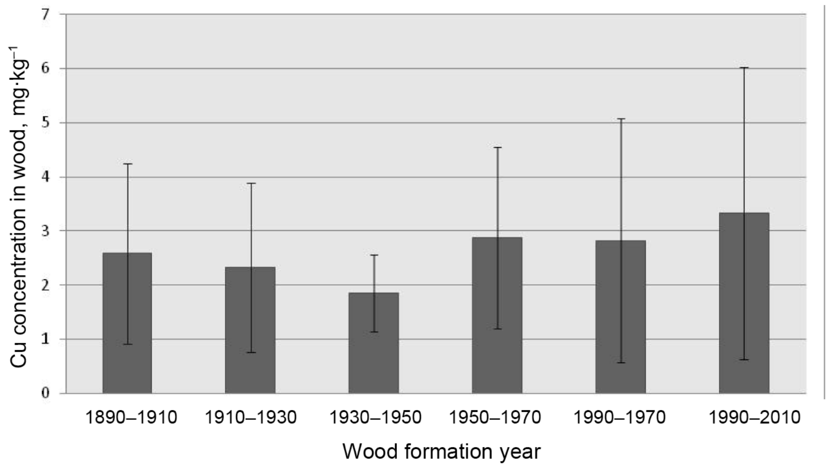


Fig. 9. Copper concentration trend in Scots pine wood formed during 1910–2010 in south-eastern Lithuania. Bars represent the mean ± SD of d.w.

7.33 ± 3.30 mg·kg^{-1} (n = 15 of d.w.); 6.88 ± 3.64 mg·kg^{-1} (n = 27 of d.w.); 7.20 ± 4.08 mg·kg^{-1} (n = 37 of d.w.); 8.25 ± 5.39 mg·kg^{-1} (n = 42 of d.w.) and 7.26 ± 4.38 mg·kg^{-1} (n = 38 of d.w.).

3.2.2. Copper trend in Scots pine tree-rings

In comparison with Zn, copper concentration from the pith towards the bark increases more rapidly (Fig. 9). No significant difference among tree-ring sections (ANOVA test, $p > 0.05$) was determined. The maximum difference in values was determined between tree-ring sections of 1930–1950 and 1990–2010 and was equal to 44.75% (Fig. 10).

In sections of 20 tree-rings, the average values in the period of 1980–2010 distributed as follows: 2.58 ± 1.67 mg·kg^{-1} (n = 4 of d.w.); 2.33 ± 1.50 mg·kg^{-1} (n = 14 of d.w.); 1.84 ± 0.71 mg·kg^{-1} (n = 25 of d.w.); 2.88 ± 1.67 mg·kg^{-1} (n = 38 of d.w.); 2.82 ± 2.25 (n = 41 of d.w.) mg·kg^{-1} and 3.33 ± 2.69 (n = 39 of d.w.) mg·kg^{-1}.

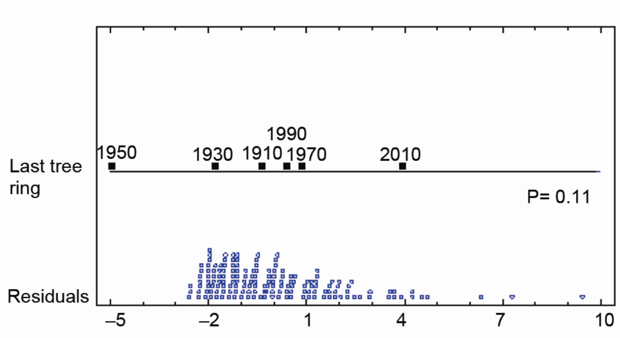


Fig. 10. Graphical ANOVA shows the distribution of Cu concentration (mg·kg^{-1} of d.w.) mean values of separate tree-ring sections

3.3. Tree age and concentration rate

Zinc concentration in Scots pine wood significantly correlated with tree age, $r = 0.50$, $p = 0.0004$ (the significant value is $p < 0.05$) (Fig. 11). In case of Cu, dependence of concentrations on tree age were statistically significant as well, i.e. $r = 0.34$, $p = 0.002$ (Fig. 12).

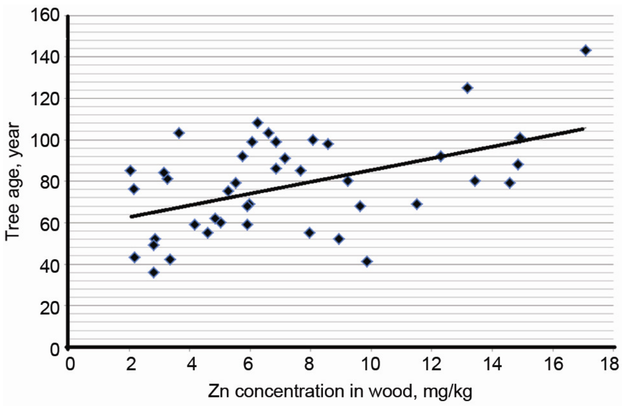
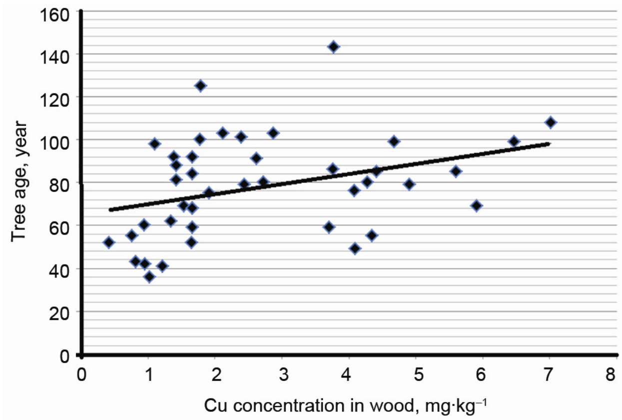


Fig. 11. Relationship between tree age and average Zn concentration in Scots pine wood



Fig, 12. Relationship between tree age and Cu concentration in Scots pine wood

In case of Cu, the most significant difference was found between trees aging from 70 years rather than between younger trees ($p = 0.03$). The average Cu concentrations in trees of different age differed from 1.98 ± 1.57 mg·kg^{-1} in trees younger than 70 years to 3.13 ± 1.67 mg·kg^{-1} in trees older than 70 years.

In case of Zn, the most significant difference was determined between trees younger than 80 years and trees older than 80 years (p = 0.008). The average Zn concentration in trees younger than 80 was equal to 5.57 ± 2.73 mg·kg^{-1}, meanwhile in trees older than 80 years it amounted to 8.70 ± 4.38 mg·kg^{-1}.

4. Discussion

Certain metals (such as Cu and Zn) are important nutritious elements for plants, thus at older age higher concentrations should be reach. Therefore, Zn and Cu concentration should be higher in older trees than in younger ones. Our results confirmed this statement by comparing amounts of accumulated Cu and Zn in tree wood with the age of trees.

The other important factors influencing TMs uptake by trees are soil properties and in particular – the soil pH and the total organic carbon. According to the obtained study results, no statistically significant dependence was determined between Zn and Cu concentrations and the soil pH or the organic carbon content.

According to Butkus and Baltrėnaitė (2007), results of trace elements accumulated in Scots pine growing at potentially contaminated sites on sand and sandy loam soils in the case of Zn reached 75 mg·kg^{-1} and Cu – 3 mg·kg^{-1}. Cu values found in similar growing conditions abroad were in the range of 0.15 – 1.02 mg·kg^{-1} (Padilla, Anderson 2002). The phytotoxic effect is evident when Cu concentration reaches 20–100 mg·kg^{-1} and Zn concentration amounts to 300–600 mg·kg^{-1} and causes the Fe deficiency in tissues (Allen 1989; Kabata-Pendias, Pendias 2001).

In all studied trees, the concentrations of both TMs did not reach any significant anomaly concentrations. In the biggest percentage of places, the Zn concentration in Scots pine wood did not reach 6 mg·kg^{-1} (n = 21). In the remaining larger part of sampled trees, the Zn values did not exceed 10 mg·kg^{-1} (n = 13). The most outstanding Zn concentrations (>10 mg·kg^{-1}), compared with all obtained values, were recorded at the 5th, 15th, 18th, 31st, 32nd, 33rd and 36th sampling places. The bigger part of higher Zn values could be related to age of trees as these concentrations were found in trees older than 80 years. However, at the 33rd site, Zn concentration (11.52 ± 3.53 mg·kg^{-1}; tree age = 69 years) was higher than expected; however, it corresponds with concentrations determined in the two nearby sampling sites (the 32nd and the 31st), which suggest the presence of higher Zn concentration in that part of the territory.

In the majority of investigated sites, Cu concentration in Scots pine wood did not reach 2 mg·kg^{-1} (n = 22). The second category would be the sites where Cu concentration in Scots pines did not exceed 4 mg·kg^{-1} (n = 9). Finally, the outstanding Cu concentrations, compared with all results, ranged from 4 to 8 mg·kg^{-1} (n = 11). As well as in the case with Zn, the bigger concentrations of Cu in Scots pine were found in older trees. However, two sites could be excluded, i.e. the 22nd (4.35 ± 1.13 mg·kg^{-1}; tree age = 55 years) and the 34th (4.10 ± 1.24 mg·kg^{-1}; tree age = 49 years). Both sites are located in Lazdijai County where, according to Mažvila (2001), Cu concentration in soil is two times higher if compared with the entire investigated territory.

The results of radial tendencies of Zn and Cu concentrations in Scots pine stem showed a slight increase from the pith towards the bark. Watmough (1999) – after reviewing different dendrochemical studies – and Larison and Helmisaari (1998) – after their study – remarked that concentrations of essential elements such as Cu and Zn have the tendency to increase towards the bark.

An important tendency of minimum concentrations of both investigated trace metals being determined during the period of 1930–1950 was also noticed. Interestingly, if compared with normal conditions, more frequent extreme heat waves and cold periods which lasted for longer were recorded during the period of 1930–1960 (Bukantis 1994). It could be assumed that during the period 1930–1960, the uptake of TMs was disturbed by the retarded increase in wood formation.

5. Conclusions

1. The background Zn concentration accumulated in Scots pine stem wood in the south-eastern part of Lithuania is found to equal to 7.2 mg·kg^{-1} and the background concentration of Cu is 2.5 mg·kg^{-1}. The estimated minimal anomaly concentrations of Zn is 21.3 and of Cu – 9.0 mg·kg^{-1}.
2. The results of natural radial tendencies in Cu and Zn elements in Scots pine stem wood did not reveal any statistically significant concentration spikes in any of the investigated tree-ring sections. However, in the wood formed during the period of 1930–1950, the smallest concentrations of both investigated metals were observed (6.8 mg·kg^{-1} of Zn compared with average 7.4 mg·kg^{-1}, and 1.8 mg·kg^{-1} of Cu while the average concentration is 2.6 mg·kg^{-1}).
3. A significant relationship with Zn and Cu concentrations was found between ages of trees. The most significant difference in Cu concentrations was determined between trees younger and older than 70 years (the difference amounting to 36.7%); in the case of Zn, the most significant difference was determined between Scots pine trees younger and older than 80 years old (the difference amounting to 35.9%).
4. To determine the possible anthropogenic impact related to higher release of Cu and Zn into the environment, it is recommended to precisely evaluate the age of a tree in order to avoid mistakes in interpretation of dendrochemical results.

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VARIO IR CINKO KONCENTRACIJOS KAUPIMOSI TENDENCIJOS *Pinus sylvestris* L. METINĖSE RIEVĖSE TYRIMAI IR VERTINIMAS

P. Baltrėnas, D. Vaitkutė

S a n t r a u k a

Viena iš aktualių nūdienos aplinkosaugos problemų yra sunkieji metalai, tad tampa vis svarbiau kuo išsamiau įvertinti jų sklaidą ir kaupimąsi gamtinėse sistemose. Šiems tyrimams pasirinkta paprastoji pušis (*Pinus sylvestris* L.). Dėl paprastos medienos sandaros, aiškiai matomų metinių rievių, tinkamumo metalų koncentracijų kitimui įvertinti laikui bėgant tai yra paranki medžių rūšis aplinkai sukeliamam stresui nustatyti. Pirminiam vertinimui atlikti pasirinkta viena iš miškingiausių Lietuvos vietovių – Pietryčių Lietuva. Iš gautų rezultatų galima teigti, kad Pietryčių Lietuvoje paprastosiose pušyse Zn foninis kiekis yra 7,2 mg·kg^{-1}, o Cu – 2,5 mg·kg^{-1}. Taip pat buvo apskaičiuotos šių metalų minimalios anomalios koncentracijos: Zn – 21,3 mg·kg^{-1}, o Cu – 9,0 mg·kg^{-1}. Zn ir Cu metinėse pušies rievėse buvo pasiskirstęs tolygiai, šiek tiek koncentracijos didėjo žievės link. Taip pat pastebėta, kad metinėse rievėse, susiformavusiose 1930–1950 m., abiejų metalų koncentracija, palyginti su kitų rievių, yra šiek tiek mažesnė. Tai gali būti siejama su 1930–1960 m. vyravusių itin ekstremalių orų laikotarpiu.

Reikšminiai žodžiai: cinkas, varis, Pietryčių Lietuva, paprastoji pušis (*pinus sylvestris* L.), metinės rievės, foninės koncentracijos.

ИССЛЕДОВАНИЕ И ОЦЕНКА ИЗМЕНЕНИЙ КОНЦЕНТРАЦИЙ МЕДИ И ЦИНКА В ГОДОВЫХ КОЛЬЦАХ *Pinus sylvestris* L.

П. Балтренас, Д. Вайткуте

Р е з ю м е

Одной из актуальных современных экологических проблем являются тяжелые металлы, поэтому представляется всё более важным исследовать их рассеяние и аккумуляцию в природных системах. Для исследования фонового накопления тяжелых металлов древесиной сосны обыкновенной (*Pinus sylvestris* L.) были выбраны деревья, произрастающие на техногенно ненарушенных территориях. Для первичной оценки была выбрана одна из наиболее лесистых местностей Литвы – юго-восточная Литва. На основании полученных результатов можно утверждать, что в юго-восточной Литве в древесине сосны обыкновенной фоновая концентрация Zn составляет 7.2 мг/кг, Cu – 2.5 мг/кг. Концентрации цинка и меди в годичных кольцах сосны разделились поровну со слегка выраженным ее увеличением в направлении коры. Было также отмечено, что в годовых кольцах, сформировавшихся в 1930–1950 годах, концентрации обоих металлов по сравнению с другими годовыми кольцами роста несколько меньше, что может быть связано с господствовавшими в 1930–1960 годах экстремальными погодными условиями.

Ключевые слова: цинк, медь, юго-восточная Литва, сосна обыкновенная, годовые кольца, фоновые уровни.

Pranas BALTRĖNAS. Dr Habil, Prof. and head of the Dept of Environmental Protection, Vilnius Gediminas Technical University (VGTU). Doctor Habil of Science (air pollution), Leningrad Civil Engineering Institute (Russia), 1989. Doctor of Science (air pollution), Ivanov Textile Institute (Russia), 1975. Employment: Professor (1990), Associate Professor (1985), senior lecturer (1975), Vilnius Civil Engineering Institute (VISI, now VGTU). Publications: author of 13 monographs, 24 study-guides, over 320 research papers and 67 inventions. Honorary awards and membership: prize-winner of the Republic of Lithuania (1994), a corresponding Member of the Ukrainian Academy of Technological Cybernetics, a full Member of International Academy of Ecology and Life Protection. Probation in Germany and Finland. Research interests: air pollution, pollutant properties, pollution control equipment and methods.

Dovilė VAITKUTĖ. PhD student, Assistant to the Dept of Environmental Protection, Vilnius Gediminas Technical University. Research interests: biomonitoring, geochemistry, dendrochemistry, environmental impact assessment.