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MANGANESE TRENDS IN TREE RINGS OF *PINUS SYLVESTRIS* L. – MONITORING SOIL CHEMICAL CHANGES

Dovile Vaitkute[1], Pranas Baltrenas[2]

[1,2]*Vilnius Gediminas technical university, Saulėtekio ave. 11, LT-10223 Vilnius, Lithuania.*
E-mails: [1]dovilev@vgtu.lt; [2]pbalt@vgtu.lt

Abstract. Dendrochemistry can be used to monitor historical changes of the elemental composition in the polluted or undisturbed areas. In this study for analysis were taken the increment cores of Scots pine (*Pinus sylvestris* L.) from South – Eastern part of Lithuania. This region has one of the biggest pine forest areas in Lithuania, and was chosen to determine the background concentrations of manganese (Mn) in Scots pine tree rings. The particular analysis from uncontaminated areas may help to determine the elemental changes in tree rings at potentially polluted sites. Mn concentrations changes also could be used to reconstruct the pH historical changes in the investigated area soils. Current analysis results revealed that Mn concentration negatively correlated with soil pH and organic carbon, also slightly decreases from the tree heartwood to sapwood.

Keywords: tree rings, manganese, soil, pH, organic carbon, pine.

1. Introduction

Dendrochemical analyses of trees can be beneficial in the reconstruction of the past events of the environmental effects and the changes in the availability of elements and effects of pollution (Padilla and Anderson 2002; Augustin *et al.* 2005; Stravinskienė and Erlickytė – Marčiukaitienė 2009). For reconstruction of pollution events with heavy metals as Pb, Cu, Ni, Zn *and others* or radioactive isotopes in temperate climate has been successfully applied coniferous tree species, which have well distinct tree rings (Watmough and Hutchinson 1999; 2002; Orlandi *et al.*, 2002; Lageard *et al.* 2008; Kuang *et al.* 2007; Baltrėnaitė *et al.* 2010; Pliopaitė Bataitienė and Butkus 2010). Tree rings has been also applied for the reconstruction of the changes in soil chemistry (Guyette and Cutter 1994; Augustin *et al.* 2005; Gauthier *et al.* 2007). For example, manganese (Mn) concentration trend in tree rings can indicate the essential changes in rooting zone (Augustin 2009).

Manganese is essential for many plant functions, for example, the assimilation of carbon dioxide in photosynthesis, the synthesis of chlorophyll and in nitrate assimilation, activation of fat forming enzymes, formation of riboflavin, ascorbic acid, and carotene. However, the toxicity effect of Mn to plants is not so common environmental problem, because Mn bioavailability to plants increases only then when the soil pH is in range from 5 to 4.2 (Lindsay 1979; Guyette and Cutter 1994; Bukata and Kyser 2007; Augustin *et al.* 2005; Augustin 2009) (1).

$$Mn_3O_4 + 8H^+ + 2e^- \leftrightarrow 3Mn^{2+} + 4H_2O \qquad (1)$$

The potential Mn^{2+} increases 100 times for each unit change in soil pH (2) (Lindsay 1979):

$$\text{Log}_{10}\, Mn^{2+}\,(aq) = 8.65 - 2pH \qquad (2)$$

The decrease of soil pH causes the loss of the base cations Ca, Mg, K and increase in the concentrations of Mn, Al and Fe – acidic cations (Augustin *et al.* 2005; Augustin 2009). When the soil pH decreases and reaches 4.2 begins the dissolution of Al oxides which are toxic elements to plants (Mossor-Pietraszewsk 2001).

Thus the Mn concentration in tree rings could indicate the period when the brake point in soil acidity appears. According to other authors, the trends of Mn and Ba was determined as a useful tool in order to reconstruct the changes in soil acidity due to acidifying elements emissions to atmosphere such as sulphur oxides (Guyette and Cutter 1994).

However, to date precisely soil acidity could be complicated because of the lack of the environmental changes historical data in the investigated sites. However, tree biggest uptake of macronutrients appears in their early ages and this leads to forest soil pH decrease with the age of the trees increasing in the forest stand (Berger *et al.* 2004). In this case the turning point for the time when soil reaches the critical threshold of pH 4.2, below which acid stress to trees become possible, could be determined. However, this method doesn't show such a significance when the sites soil is more alkaline (Ruppert and Wischow 2006).

The application of tree rings to environment monitoring is important when there is no possibility to perform the instrumental monitoring. However, tree is not a passive chemical element absorbent because the uptake of them depends on different environmental conditions and the application of trees should be cautious (Ruppert and Wischow 2006).

In this study we determined the background Mn concentrations in South – Eastern Lithuania. Additionally, analysed the Mn trends in Scots pine tree rings according to tree age and soil properties.

2. Materials and Methods

2.1. Study site

In order to determine the background concentrations of Mn in Scots pine trees was chosen one of the most forested and anthropogenic undisturbed area – the South-Eastern part of Lithuania. This is eco-region named as Dzūkų and Sūduvos Highlands (Fig 1).

The chosen study region area covers 4569.6 km^2 of Lithuania. The region dominant soil type is poor in nutrients sand and sandy loam. The climate – continental where annual precipitation varies from 550 to 700 mm.

The background Mn concentrations in Lithuanian sand and sandy loam soils vary from 372 to 419 mg/kg (Kadūnas 1998). In Varėna County (Fig 1(b)) total Mn concentration in topsoils vary from 305 to 508 mg/kg; in Lazdijai (Fig 1(a)) from 407 in some places reaches 813 mg/kg and in Trakai County (Fig 1(c)) Mn concentration ranges from 305 to 813 and more mg/kg (Kadūnas 1999).

These three Counties varies in forest cover percentage (Varėna – 69, Trakai – 47.7 and Lazdijai – 34.9 %), agriculture (22.2; 32.7 and 45.2 %) and in the built up area percent (1.2; 2.0 and 2.1 %). In this region the most anthropogenic undisturbed county is Varėna, the second – Trakai and the most anthropogenic touched Lazdijai.

The forest in this region covers about 36 % of the total area and Scots pine forests contents approximately 66 % of the total forest area.

2.2. Sampling and sample preparation for analysis

In total for the Mn analysis in tree rings were samples 42 Scots pine trees. The tree age average is 77±22 years.

Sampling was performed in the sampling grid in 10x10 km plots. In each plot was sampled one Scots pine tree. Tree core samples were taken from 1.3 m at stem height with 12 mm diameter Haglöf Presler borer. Two cores were taken per one tree. To avoid anthropogenic distribution whole sampled trees were sampled in bigger than 0.5 ha forest areas, 200 m from main roads and settlements.

Tree corers were put in paper straws and brought to laboratory for further analysis. Tree cores were air dried and sanded. After tree ring counting each core was divided in to 20 tree ring sections. These tree sections were burned in 400 ^{o}C for 6 hours.

2.3. Soil properties analysis

Soil pH was measured in 0.01 M $CaCl_2$ solution by using a digital pH meter (pH 538 WTV). The 15 g of soil sample was diluted with 75 ml of deionised water and shaken for 1 hour.

The organic carbon content was analyzed with total organic carbon analyzer (TOC-V by SHIMADZU) in 900 ^{o}C temperature.

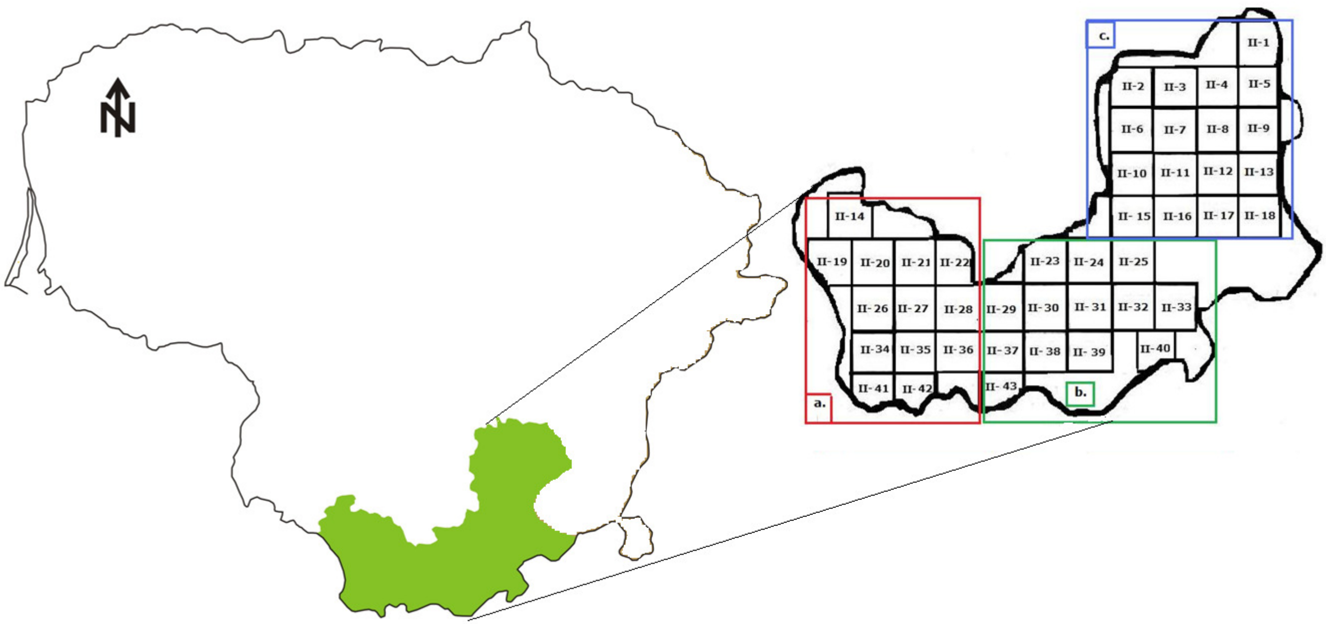

Fig 1. Study site location in Lithuania and Scots pine sampling grid divided in smaller regions (a) Lazdijai County (n=13); b) Varėna County (n=13) and c) Trakai County (n=17))

2.4. Mn determination in tree rings

Total Mn analysis in Scots pine wood and separate tree rings sections were performed with *Buck Scientific 210 VGP* Atomic Absorption Spectrophotometer (FAAS) after ash burning and mineralizing in HNO_3:H_2O_2 (10ml:2ml; 65 % and 37 %) extraction solution with ETHOS mineraliser (*Milestone*).

2.5. Statistical analysis

Each tree sample was measured in duplicate. The basic statistical data analysis (mean, standard deviation), multi-regression analysis *and other* were carried out using the *Statistica* 7.0 and *Excel 2007* program tool package. The special distribution of data was performed with *Surfer 3.2*.

3. Results and Discussion

The background average Mn concentrations in Scots pine trees in the investigated area was equal to 23.59±12.17 mg/kg and concentration average ranges from 19.8 to 27.5 (Fig 2).

The minimum determined concentrations were 3.06±0.81 and maximum 55.26±12.15 mg/kg. Such Mn concentration range in tree rings is assumed to be related with soil properties difference in investigated territory regions (Fig 9).

3.1. Does the Mn concentration shows the trend in Scots pine tree rings?

The average manganese concentration in all investigated Scots pine tree rings slightly decreased and more rapid decrease was noticed from 1890s to 1950s (Fig 3).

The results distributes in the following sequence: in year (yr) rings Mn concentration equal to 1910 – 1930 yr rings – 28.92 ± 10.19 mg/kg (n=9); in 1930 – 1950 yr rings – 26.25 ± 8.97 mg/kg (n=28); in 1950 – 1970 yr rings – 25.35 ± 9.72 (n=31); in 1970 – 1990 yr rings equal to 23.09± 9.89 and in 1990 – 2010 yr rings – 21.03± 9.20 mg/kg (n=31).

For detail analysis we excluded three trees which were growing on more alkaline soils, than the rest of the trees in the chosen part of Lithuania, and watched the Mn concentration changes during the time period (Fig 4). It was interesting to notice that the trend goes differently than in trees growing on acidic soils. Mn concentration starts to decrease from 1950s to 1970-80s and then again starts increase from 1990s to recent years. Comparing with average Mn concentration trend in tree rings from more acidic soil of whole territory, Mn concentration slightly decreased from 1960s to 2000.

3.2. Does Mn concentration in Scots pine rings depends on tree age?

The chosen site has the similar soil type and properties and climatic conditions over whole investigated area. These conditions gave us possibility to assess the Mn concentration variations in tree rings of different age Scots pine trees.

The Mn concentrations in <u>40 year</u> old pine trees rings varied from 20.78 ± 5.81 in 1970 – 1990 to 16.70 ± 3.50 mg·kg^{-1} in 1990 – 2010 year section (average of 3 Scots pine) (Fig 5).

The average values of Mn concentrations in <u>60 year</u> old trees varied from 32.14 ± 10.32 in 1950 – 1970 year section to 25.83 ± 5.35 in 1970 – 1990 and 22.44 ± 7.07 mg/kg in 1990 – 2010 year section (Fig 6).

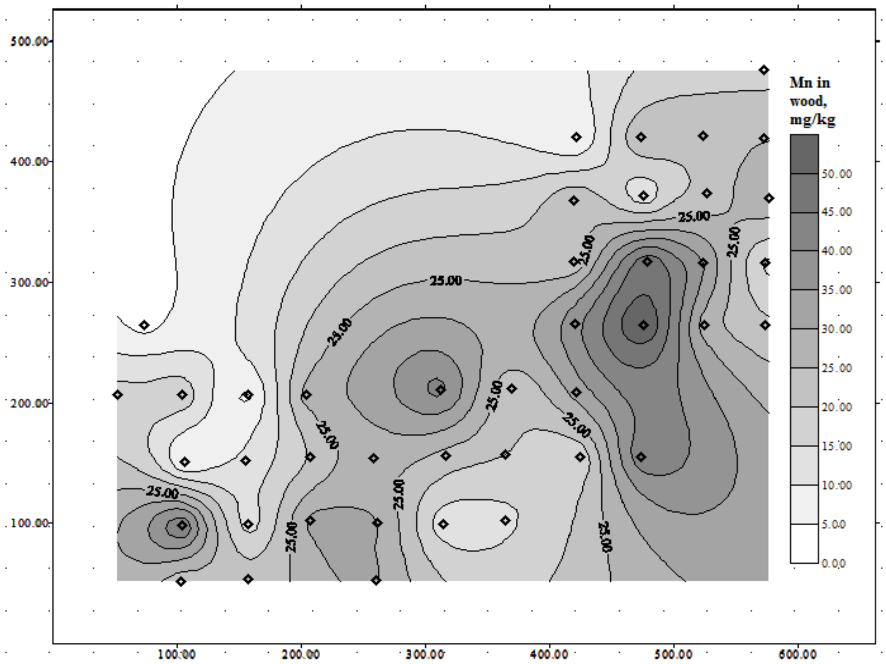

Fig 2. Mn concentrations in Scots pine spatial distribution

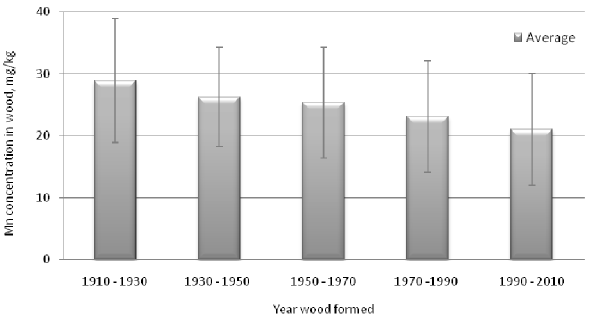

Fig 3. Mn average concentration in Scots pine tree rings. Bars represent average value of 42 samples ±SD

Fig 4. Average Mn concentration in tree rings, grown on the soil pH >7. Bars represent average value of 3 samples ±SD

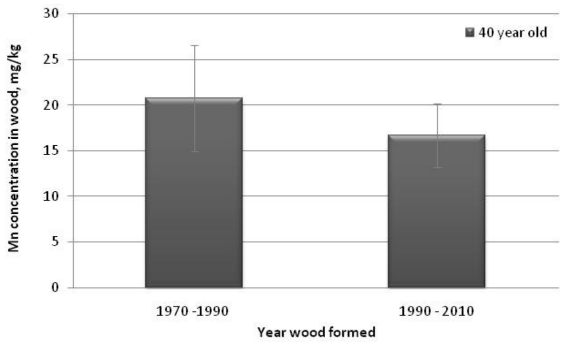

Fig 5. Mn concentration trend in 40 year Scots pine tree rings, mg·kg^{-1} (n=3 of d.w.)

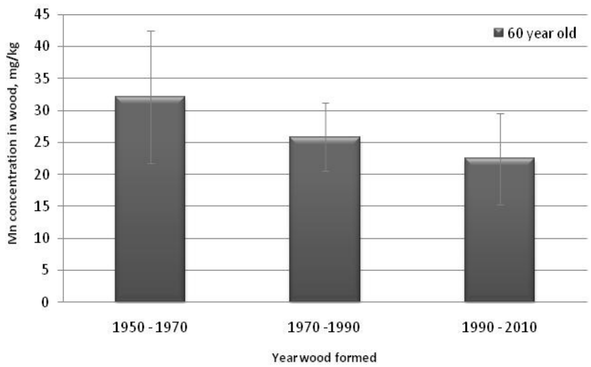

Fig 6. Mn concentration trend in 60 year Scots pine tree rings, mg·kg^{-1} (n=11 of d.w.)

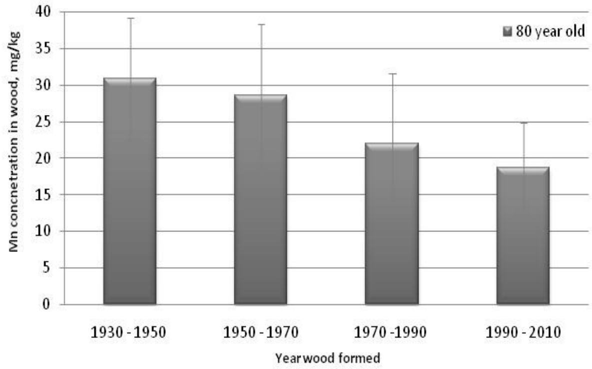

Fig 7. Mn concentration trend in 80 year Scots pine tree rings, mg·kg^{-1}(n=12 of d.w.)

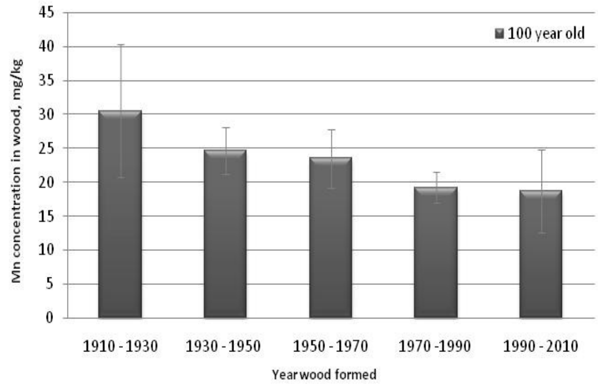

Fig 8. Mn concentration trend in 100 year Scots pine tree rings, mg·kg^{-1}(n=9, d.w.)

In the tree of 80 year old tree there was determined the decrease of Mn concentrations from 1980s to 2000 (taken middle points of the section) tree rings. This could indicate the rapid soil pH change in this time span. In 1930 – 1950 tree rings the Mn concentration determined to be 30.90±8.27 mg/kg; in 1950 – 1970 – 28.54 ± 9.85 mg/kg; in 1970 – 1990 – 22.00 ± 9.58 and in 1990 – 2010 year rings equal to 18.68 ± 6.27 mg/kg (Fig 7).

The data trends showed that decrease of Mn concentrations in tree rings starts from approximately 1960's.

In the tree of 100 year old tree the trend was similar and distributed following: in 1910 – 1930 formed wood Mn concentration is 30.51 ± 9.76 mg/kg; in 1930 – 1950 – 24.68 ± 3.44; 1950 – 1970 23.50 ± 4.25; 1970 – 1990 19.23±2.29; 1990 – 2010 – 18.68 ± 6.14 mg/kg (Fig 8).

Interesting to notice that two studies of Mn dendrochemical analysis in Germany and China performed similar Mn in tree rings trends data. In Augustin et al. 2005 study of Mn in Norway spruce trees in Germany was determined the rapid decline in Mn concentration from 1968 to 1980s (from 400 – 600 mg/kg to 50 – 100 mg/kg). In Kunang *et al.* (2008) study of Mn concentrations in Masson pine in China the Mn concentration slightly decreases from 1950s in more acid soils (were Al exchangeable concentration is higher that Mn) and in another site (where Mn mobile concentration was higher in soil) decreases rapid from 1965 to 1985.

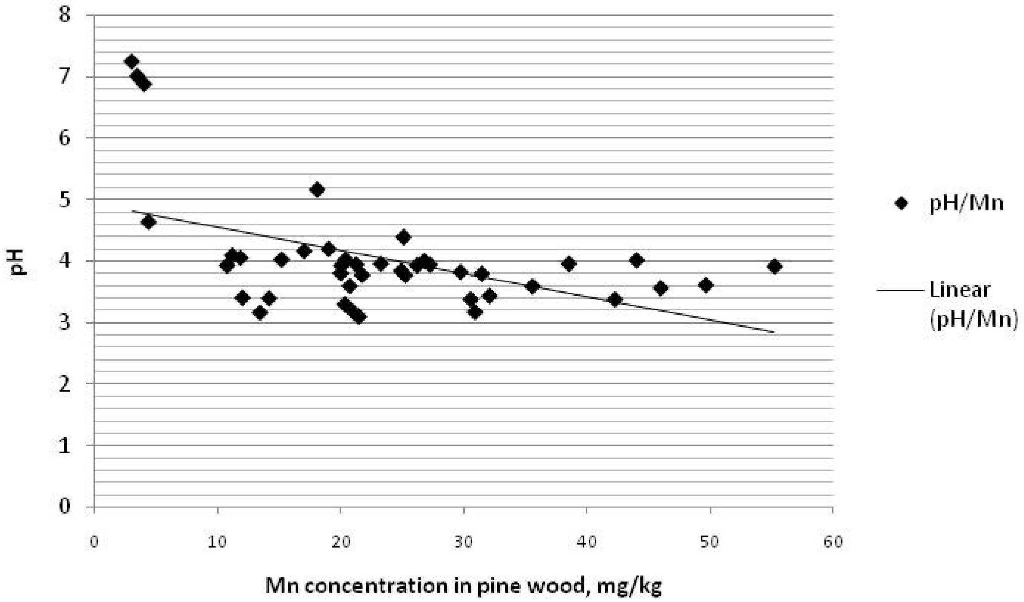

Fig 8. Mn concentration in Scots pine tree rings negative correlation with soil pH

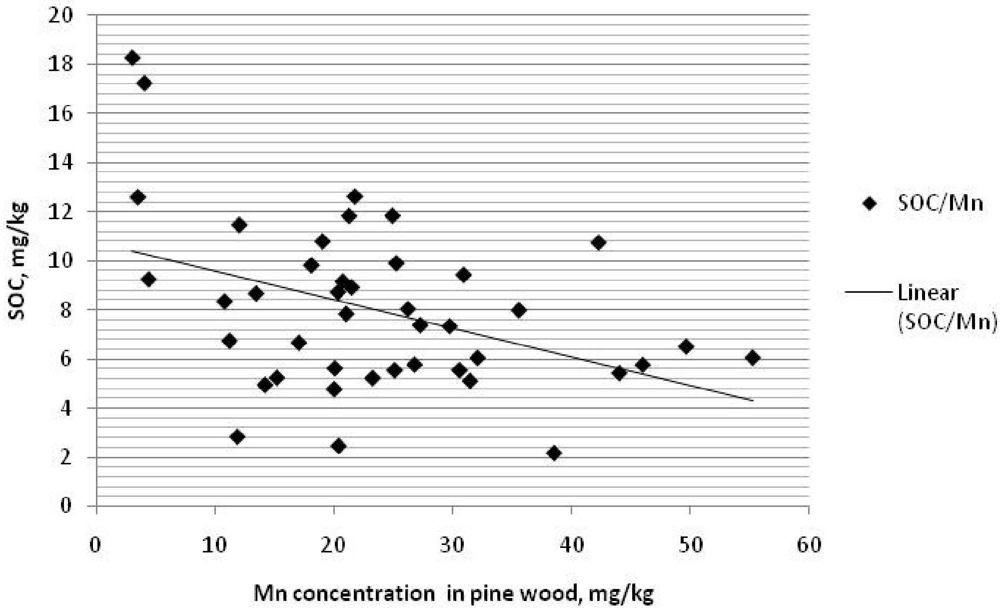

Fig 9. Mn concentration in Scots pine tree rings negative correlation with soil organic carbon (SOC)

Table 1. Soil properties and Mn concentration in tree rings of three regions in South – eastern part of Lithuania

Name	Trakai, n=17	Varėna, n=12	Lazdijai, n = 13
pH	3.92±0.47	3.68±0.34	4.08±0.94
SOC, mg/kg	8.06±2.62	6.68±2.35	8.03±3.49
Mn, mg/kg	26.00±12.92	25.97±4.51	18.24±11.17
	Correlation factors		
pH/Mn	-0.22	-0.26	**-0.70**
SOC/Mn	**-0.45**	**0.53**	**-0.73**
pH/SOC	0.03	**-0.65**	**0.83**

3.3. Does the Mn concentration in Scots pine depend on soil pH and SOC?

After performing of multi – regression analysis there was determined significant negative correlation of Mn concentration in investigated Scots pine tree rings with the soil pH values in investigated sites ($r = -0.42$, $p < 0.05$; $n = 42$) (Fig 8).

The negative correlation between Mn concentrations in tree rings and soil pH was determined in these studies: Guyette and Cutter 1994; Augustin *et al*. 2005; Ruppert and Wischow 2007; Bukata and Kyser 2007; Gauthier *et al.* 2007; Kuang *et al.* 2008; Augustin 2009.

There was also determined the statistically significant negative correlation between Mn concentration in tree rings and SOC ($r = -0.48$; $p < 0.05$, $n = 42$) (Fig 9).

3.4. Does the Mn concentration in Scots pine vary among Counties?

The investigation site was split in three different regions according to biggest administrative regions: Trakai, Varėna and Lazdijai (Fig 1). Varėna County considered to be as the most anthropogenic undisturbed among these counties. However, the Mn concentration did not differ significantly from Trakai and Lazdijai Counties. Varėna has the most acidic soil and is poor in organics, which indicated the organic carbon content, comparing with other two counties. Both Trakai and Lazdijai have the same content of organic carbon. However, Trakai County varies a bit more acidic soil than in Lazdijai (Table 1).

Thus, all three counties varied in soil pH and SOC amount. The most varied soil conditions (highest SD of pH and SOC) were performed in Lazdijai. It is great probability that such heterogenic conditions could influence the greater correlation factors between pH, SOC and Mn concentrations in this site. It is interesting to notice that in Varėna region Mn concentration in tree rings correlates significant positively with SOC and in other two counties correlation is negative. However, in the Varėna County soil organic carbon average is less than in other two. There might be assumed that only particular soil carbon concentration in the soil can have a negative impact on Mn uptake by trees. This could be evaluated during the further investigation including the other Lithuania territories with different soil type.

4. Conclusions

1. Comparing Mn concentration between Scots pine trees of different age was determined that the Mn concentrations tends to decrease from the 1960s. These trends could indicate the soil conditions changes in this period which could be related with stands aging process, soil loss of macronutrients, even the anthropogenic influence as emission of acidifying compounds.
2. The Mn concentration trend in tree rings showed similar tendencies – slight decrease from 1960's - comparing our study with other authors who made their analysis with Norway (Germany) and Masson pines (China).
3. This study let us assume that Scots pine growing in site with different soil pH values varies not only in the amount of accumulated Mn but also in the accumulation trends. The more detailed analysis should be done to confirm this assumption.
4. The obtained study results revealed that Mn concentration in tree rings significantly negatively correlates with currently determined soil pH and also soil organic carbon.

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