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METALS ACCUMULATION IN SCOTS PINE (*PINUS SYLVESTRIS* L.) WOOD AND BARK AFFECTED WITH ENVIRONMENTAL POLLUTION

Donata Krutul, Tomasz Zielenkiewicz, Andrzej Radomski, Janusz Zawadzki
Andrzej Antczak, Michał Drożdżek, Tomasz Makowski
Warsaw University of Life Sciences
Department of Wood Science and Wood Protection
Nowoursynowska 159
02-776 Warsaw
Poland

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ABSTRACT

Studies on the content and distribution of mineral substances including calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn), iron (Fe), sodium (Na), zinc (Zn), aluminum (Al), lead (Pb) and strontium (Sr) were performed. Samples of Scots pine were gained from stems with Ist degradation degree of tree (considered to grow in the area with weak environmental pollution), IInd degradation degree (strong pollution) and IIIrd degradation degree (very strong pollution). Nitrogen industrial plant was acknowledged as the source of pollution. Samples were collected from butt-end, middle- and top sections of the stem in following zones: sapwood, heartwood adjacent sapwood, heartwood and bark. Results indicate that nitrogen industrial plant causes the decrease of mineral substances content in bark from butt-end section of stems with IInd and IIIrd degradation degree in relation to stems with Ist degradation degree. Calcium content is the highest in heartwood and decreases in the direction to stem perimeter, regardless of stem section and environmental pollution degree. Very strong pollution decreases potassium content in wood in comparison to samples collected in areas with strong and weak pollution. Environmental pollution also decreases sodium content in wood, and increases content of manganese, aluminum, lead and strontium.

KEYWORDS: Scots pine, wood, bark, mineral substances, macroelements, microelements, trace elements.

INTRODUCTION

Mineral substances content in wood and bark depends on the species, tree age and habitat, as well as on the sampling position on the cross- and longitudinal section of the stem (Rademacher et al. 1986, Krutul 1996, Krutul et al. 2006, 2010, 2011, Okada et al. 1993, Watmough et al. 1999). Significant differences in mineral substances content were denoted in pine and oak wood (cca. 100-year old) between top and butt-end section of the stem. Wood from the top section contains generally more mineral substances than wood from butt-end section. This value is many times higher in bark than in wood, but it is higher in bark from butt-end section (Krutul 1996, 1998).

According to Fengel and Wegener (1984), Loto and Fakunkun (1989) and Rademacher et al. (1986), mineral substances content in wood of the same species varies in wide range.

Content and distribution of mineral substances on the cross- and longitudinal section of stem differ and depend on factors causing environmental pollution, regardless of species (Krutul et al. 2006, 2010, Watmough et al. 1998, Watmough and Hutchinson 1999).

The presence of heavy metals, especially lead, is the measure of industrial environmental pollution (Gulson et al. 1981). Contamination with heavy metals may be caused by factors such as fuels combustion in industry, transport and household boilers. The increased content of heavy metals is observed in the top soil layer in forests growing in urban areas, in comparison to rural ones (Pouyat and McDonnel 1991, Pouyat et al. 1995).

If soil is the source of pollution, heavy metals are collected by tree through the root system, where low-mobile ions like lead (Pb) are accumulated. Where most of contaminations are originated from the atmosphere, the accumulation of more mobile cadmium (Cd) in tree sprouts is observed. The bioaccumulation indicator of all heavy metals is lower when plants grow on soils with high sorption capacity, which is dependent on colloids amount (humus) absorbing different ions including heavy metals. Accumulation indicator depends also on the soil pH – plants contamination is higher on acidic soils.

Taking into consideration that so many factors influence the distribution of mineral substances, including particular elements, on cross- and longitudinal sections of stem, there were undertake studies of mineral substances distribution changes, depending on environmental pollution degree caused by emissions from nitrogen industrial plant "Kędzierzyn" in wood and bark of Scots pine (*Pinus sylvestris* L.)

MATERIALS AND METHODS

Stems of Scots pine (*Pinus sylvestris* L.), cca. 70 year old, were collected in December from "Silesia" region in three different areas with various degree of environmental pollution. Three stems were cut in each area, which differed with tree degradation degree (defoliation). Areas of Ist, IInd and IIIrd trees degradation degree were marked out what corresponds to, respectively, weak, strong and very strong environmental pollution. Nitrogen industrial plant "Kędzierzyn" was acknowledged as the main source of pollution: the emission of ammonia in 1986 equaled 1800 tons and in 1991 even 4800 tons. In 2005 emission decreased to 500 tons.

Three cca 200 thick disks were cut from each stem (in butt-end, middle and top section). Samples from each disk were collected (on whole perimeter) from sapwood, heartwood adjacent sapwood and heartwood. Both wood and bark samples were disintegrated using laboratory mill and fractionated on sieves. Dusty fraction was used for further analysis. Mineral substances content analysis was performed on the basis of ash content after burning samples in muffle furnace (cca 3±0.0001 g of the sample was burned in 600°C until reaching of constant mass).

Samples for analysis of calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn), iron (Fe), zinc (Zn), aluminum (Al), lead (Pb) and strontium (Sr) were prepared with microwave mineralization in closed system. Determination of Ca, Mg, Fe, Zn, Al, Pb and Sr content was performed with ICP-AES method according to ZAF procedure. Content of K and Na was analyzed using GFAAS.

RESULTS AND DISCUSSION

Values of mineral substances content in wood and bark of analyzed pine with different degradation degrees are presented in the Fig. 1. Results show that regardless of pollution degree heartwood adjacent sapwood from butt-end and middle stem section contains higher or similar amount of mineral substances in relation to sapwood and 20-40% higher in comparison to heartwood. In the top section of stems with IInd and IIIrd degradation degree mineral substances content is twice higher both in sapwood and heartwood in relation to butt-end and middle stem sections. According to Krutul (1998) heartwood and sapwood of Scots pine from top section contains higher amount of mineral substances in comparison to butt-end and middle section, irrespective of tree habitat and age (80, 90 and 160 years old). Mineral substances content in heartwood is higher than in sapwood.

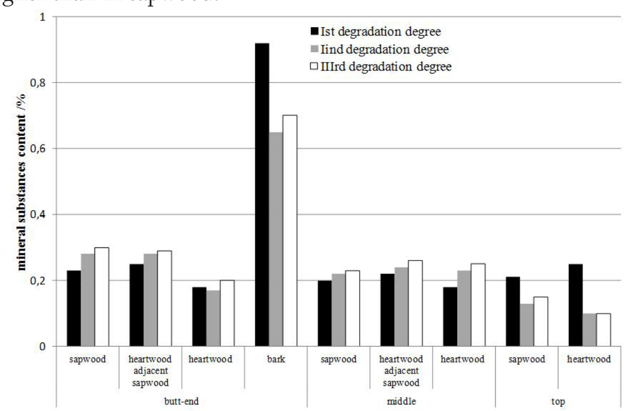

Fig. 1: Mineral substances content in the wood and bark of analyzed pine.

In analyzed stems with Ist degradation degree mineral substances content in heartwood from top section is 15 % higher in relation to sapwood.

Rademacher et al. (1986) stated that mineral substance content increases when the growing conditions of trees (*Picea abies* L.) get worse. Also in analyzed stems with IInd and IIIrd degree of degradation (strong and very strong environmental pollution) sapwood contains respectively 22% and 23% more mineral substances in comparison to sapwood with Ist degradation degree. This difference is especially significant in butt-end section (Fig. 1).

Bark from butt-end section contains from two to seven times higher amount of mineral substances in relation to wood. Mineral substances content in bark from stems with the Ist degradation degree is cca. 30% and 24% higher in comparison to, respectively, stems with the IInd and IIIrd degradation degree. Environmental pollution causes the decrease of mineral substances content in bark from butt-end section (Fig. 1).

Regardless of tree species, calcium, potassium and magnesium are metallic macro-elements with the highest content in wood.

Calcium is the element collected by plants from soil in the dissolved form of Ca2+ ion only when the soil pH is relatively low. It is transported almost only through the xylem. Its function involves the regulation of the activity of many enzymes such as ATP-ase, amylase, phospholipase and easy connects for example with cellulose, pectins as well as poly-galactouronic acid. This action decreases the cell walls elasticity. The lack of calcium leads to growth inhibition, sprouts decay and roots covering with mucus (Kopcewicz et al. 1998)

On the basis of results presented in the Fig. 2 it may be observed that calcium content in all collected stems, regardless of the degradation degree is the highest in the pith zone and decreases in the direction to the perimeter in wood from each analyzed cross-section.

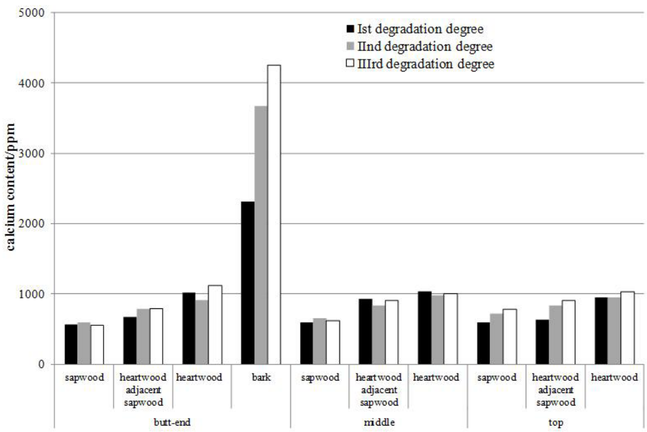

Fig. 2: Calcium content in the wood and bark of analyzed pine.

According to Krutul (1998) in 80, 90 and 160-year old pine (*Pinus sylvestris* L.) stems calcium content is higher in heartwood in comparison to sapwood and it is the highest in the top section of the stem. As it arises from Watmough et al. (1999) calcium content in pine wood increases in the direction from pith to perimeter and it is the highest in heartwood adjacent sapwood.

In analyzed pine stems only sapwood in top section of the stem contains more calcium than sapwood from butt-end section and its content is the highest in heartwood.

Calcium content in bark from butt-end section is from two to four times higher in comparison to heartwood and from three to seven times higher in relation to sapwood.

The content of calcium in bark of 110-year old Scots pine (*Pinus sylvestris* L.) in butt-end section of the stem is fivefold higher in comparison to heartwood, sevenfold higher in relation to sapwood adjacent heartwood and eightfold higher in relation to sapwood (Krutul et al. 1999).

Potassium is necessary for proper plant development and is very mobile. This is the activator of more than 50 enzymes, takes a part in osmoregulation and ion equilibrium. Its transportation is performed through both xylem and phloem (Kopcewicz et al. 1998).

Regardless the environmental pollution, potassium content in sapwood is higher than in heartwood and wood in butt-end section contains higher amount of this element in relation to the top section of the stem (Fig. 3). These observations are consistent with the data of Watmough et al. (1999) who denoted that potassium content in sapwood taken from Scots pine grown in north-west England is higher in relation to heartwood.

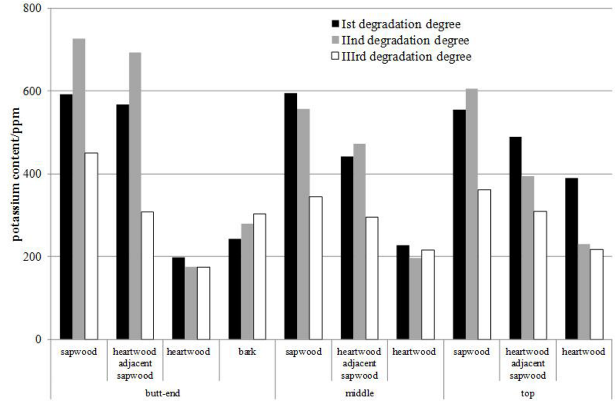

Fig. 3: Potassium content in the wood and bark of analyzed pine.

Results of Krutul (1999) show that pine stems (80, 90 and 160-year old) heartwood contains more potassium comparing to sapwood and its content is the highest in the stem top section.

Very strong environmental pollution originated from nitrogen industrial plant causes the decrease of potassium content on the cross-section of butt-end, middle and top section of the stem in relation to wood from stems with lesser degradation degree.

Potassium content in bark from the butt-end section is lower in relation to sapwood and heartwood adjacent sapwood regardless of degradation degree (Fig. 3). Bark from butt-end section of a stem with Ist degradation degree (weak pollution) contains 20% more potassium than heartwood. In bark from IInd and IIIrd degradation degree stems this difference is 40%.

Magnesium in the form of Mg^{2+} is strongly hydrated ion which is transported mainly through xylem. In cell walls it is associated with pectins. It appears to act hostile in relation to K^+ and NH_4^+ ions decreasing their collection by plants. Its transport takes place through phloem and xylem. It plays active role in ion bridges forming between ATP and enzymatic protein.

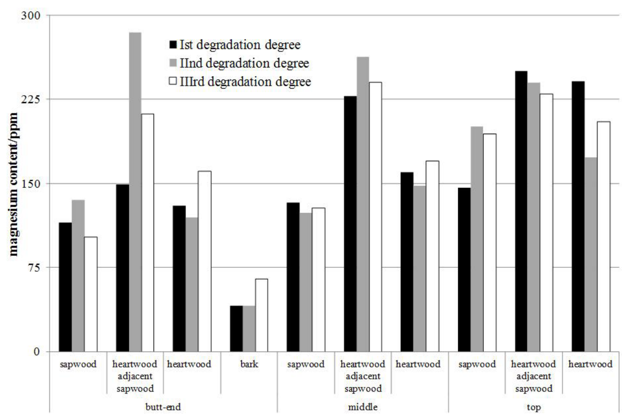

Fig. 4: Magnesium content in the wood and bark of analyzed pine.

Data presented in the Fig. 4 shows that regardless the degradation degree, heartwood adjacent sapwood contains more magnesium in relation to both sapwood and heartwood.

Watmough et al. (1999) denoted that magnesium content in Scots pine wood increases in direction from pith to perimeter with the local maximum on the sapwood and heartwood joint.

According to Krutul (1998), in 80 and 90-year old pine stems, sapwood contains more magnesium than heartwood. Magnesium content in the top section is higher in comparison to butt-end section. Differences in magnesium content in heartwood and sapwood disappear, but it is higher in the middle and top section in relation to butt-end.

Regardless the degradation degree, magnesium content in the top section of analyzed stems is higher in relation to butt-end section, what is consistent with the results of Krutul (1998).

Bark contains from two to seven times higher amount of magnesium. Bark from butt-end section of stems with IIIrd degradation degree contains 35% more magnesium comparing with stems of IInd and Ist degradation degree.

Manganese is an element which occurs on the various oxidation degree (Mn^{2+}, Mn^{3+}). It forms unstable complexes with some enzymes. Takes a part in water decomposition reaction and oxygen release in photosynthesis process, activates many enzymes participating in proteins, carbohydrates and lipids metabolism. Deficiency of manganese causes the retardation of elongation growth and side roots creation, as well as the increase of low temperatures vulnerability. Both deficiency and excess of manganese cause the decrease of auxins content.

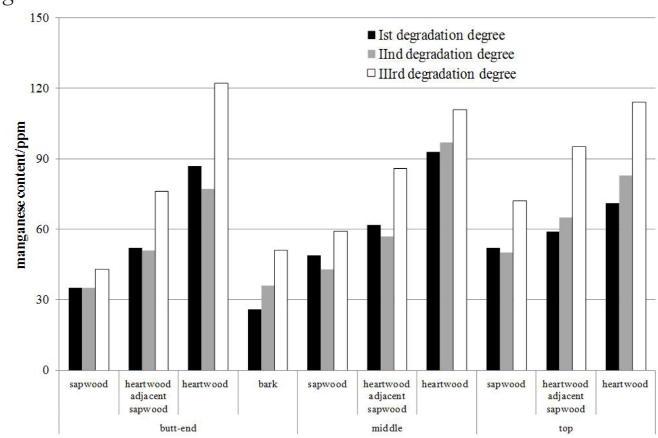

Fig. 5: Manganese content in the wood and bark of analyzed pine.

Manganese content is few-fold lower than magnesium content (Figs. 4 and 5). Regardless the degradation degree, manganese content in analyzed wood decreases in the direction from pith to perimeter, in butt-end, middle and top sections (Fig. 5). In stems with IIIrd degradation degree, wood from all zones (sapwood, heartwood, heartwood adjacent sapwood) contains 20-40% more of manganese in relation to wood taken characterized with IInd and Ist degradation degree.

According to Krutul et al. (1999), manganese content in 110-year old wood gained from non-polluted environment, both in heartwood adjacent sapwood and heartwood, as well as in bark from butt-end section is similar and equals 115 $mg\cdot kg^{-1}$, while its content in sapwood is lower and is on the level of 75 $mg\cdot kg^{-1}$. Bark in analyzed stems contains from two to four times lower amount of manganese in comparison to bark gained from the environment which was not polluted at all.

Nitrogen industrial plant causes the decrease of manganese content in sapwood, heartwood adjacent sapwood and in bark.

Iron (Fe^{2+}, Fe^{3+}, chelates) is an element which is necessary for proper plant development. It is, similarly like calcium, collected from soil when pH is low. It migrates through xylem. Iron transforms to the form inaccessible for plants when big amount of calcium occurs in soil. It participates in redox reactions as the electron carrier, or forms the ion bridge between enzyme and substrate, like magnesium and manganese. The role of the catalyst in the synthesis of some proteins and chlorophyll is especially important (Kopcewicz et al. 1998). Data presented in the fig. 6 shows that iron content in wood is the highest in Ist degradation degree stems and equals 18.4 mg/kg in heartwood and 13.8 $mg \cdot kg^{-1}$ in sapwood. Wood from the top section contains similar iron amount, regardless the degradation degree.

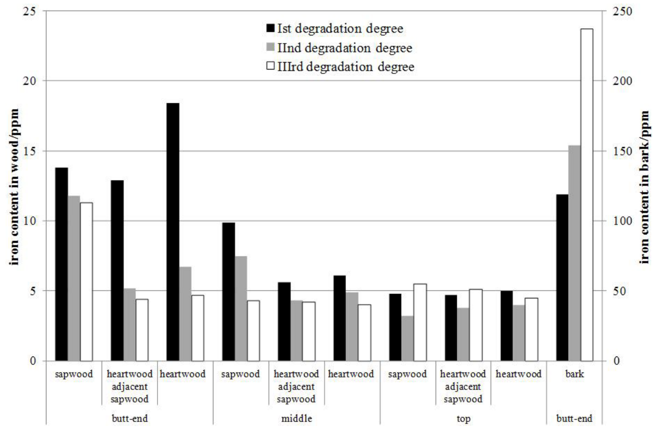

Fig. 6: Iron content in the wood and bark of analyzed pine.

According to Krutul (1998), in 90 and 160-year old pine stems top section contains more iron (33 – 86 $mg \cdot kg^{-1}$ both in sapwood and heartwood) in relation to butt-end section (20 – 62 $mg \cdot kg^{-1}$). Iron content in bark from butt-end section equals 119 $mg \cdot kg^{-1}$ for Ist degradation degree and 237 $mg \cdot kg^{-1}$ for IIIrd degradation degree. Environmental pollution related to the nitrogen industrial plant causes the increase of iron content in bark and its decrease in wood.

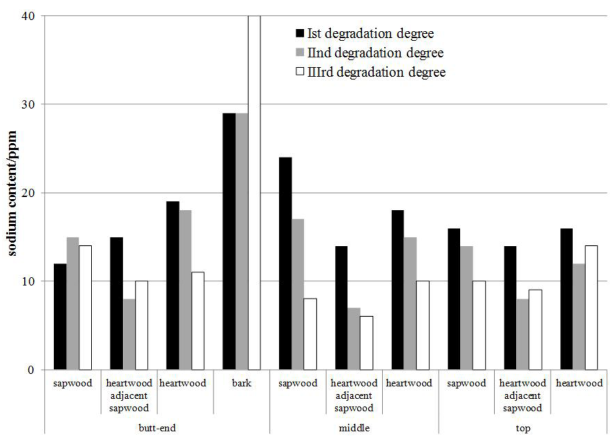

Fig. 7: Sodium content in the wood and bark of analyzed pine.

Sodium is an element which is not necessary for proper plant development, but its presence may be advantageous for life processes and it may replace potassium in some of its functions (Kopcewicz et al. 1998). Sodium content in wood of analyzed stems equals 8 – 24 mg·kg^{-1} (Fig. 7).

According to Krutul (1998), 80 and 160-year old Scots pine stems contain more sodium in heartwood (31 – 56.5 mg·kg^{-1}) than in sapwood (16 – 27 mg·kg^{-1}). Sodium content in wood from analyzed stems is almost twice lower. It is comparable to iron content value.

Sodium content in bark from butt-end section equals 29 mg·kg^{-1} for Ist and IInd degradation degree, and 40 mg/kg for IIIrd degradation degree.

Zinc is the necessary element for all plants. It influences the activity of many enzymes, participates in carbonic anhydrase, carboxypeptidase, alcohol dehydrogenase and superoxide dismutase (SOD) together with copper. It takes a part in the regulation of carbohydrates metabolism and proteins synthesis. It is the structural component of ribosomes and cell walls. Zinc and phosphorus are elements with strong hostile properties. Inappropriate ratio of these two elements causes the decrease of zinc collection (Kopcewicz et al. 1998).

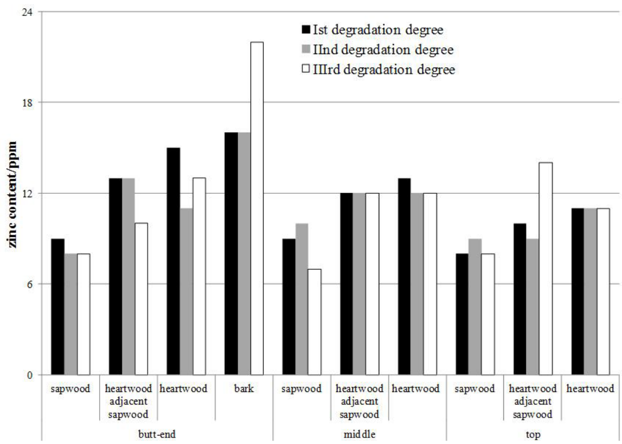

Fig. 8: Zinc content in the wood and bark of analyzed pine.

On the basis of data presented in the fig. 8, regardless the degradation degree, zinc content is similar and equals from 7 to 15 mg·kg^{-1}. Heartwood contains more zinc than sapwood.

Krutul et al. (1999) stated that in 110-year old pine wood from unpolluted environment zinc content is similar in sapwood, heartwood adjacent sapwood and heartwood and equals cca. 15 mg·kg^{-1}.

Zinc content in bark from analyzed stems with Ist and IInd degradation degree is equal to 16 mg·kg^{-1} and for III rd degradation degree this value is 22 mg·kg^{-1}, and is correspondingly 55 and 25 % lower in relation to unpolluted samples (Krutul et al. 1999).

Aluminum presence is disadvantageous for most of plants. But in case of high content of copper and manganese in soil, aluminum decreases collection of these elements, partially preserving plants against their toxic action.

On the basis of data presented in the Fig. 9, it may be stated that irrespective of degradation degree, aluminum content in butt-end and middle section decreases in the direction from pith to perimeter. In the top section of stems with Ist and IIIrd degradation degree aluminum content on the cross-section is similar.

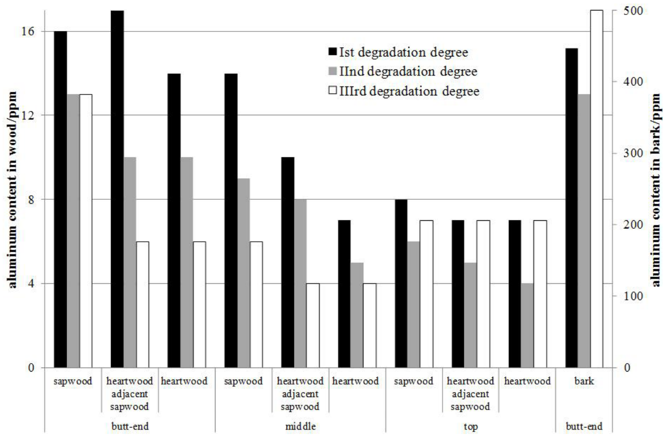

Fig. 9: Aluminum content in the wood and bark of analyzed pine.

According to Krutul et al. (1999), 110-year old pine stem contains from cca. 4 mg·kg^{-1}aluminum in sapwood adjacent heartwood to cca. 15 mg·kg^{-1} in heartwood. Aluminum content in bark from butt-end section equals 145 mg·kg^{-1}. In bark from analyzed stems aluminum content is also from dozens of to more than a hundred times higher in relation to wood. Only calcium content in bark is higher. Nitrogen industrial plant causes the increase of aluminum content in bark.

Both lead and strontium are not necessary for proper plant development. Their presence testifies the environmental pollution. Fig. 10 presents lead content in analyzed stems. Only in the middle section of stems with different degradation degrees, heartwood adjacent sapwood contains more lead in comparison to heartwood and sapwood. Lead content in butt-end and top sections is almost similar for samples with Ist degradation degree, while heartwood from stems with IInd and IIIrd degradation degree contains more lead than heartwood adjacent sapwood and sapwood.

According to Watmough et al. (1998), dependently on the environmental pollution lead content in annual rings of sugar maple varies from 0.5 to 1.5 mg·kg^{-1}. Watmough and Hutchinson (2002) stated that lead content is increased on the joint of sapwood and heartwood. The highest lead content was stated in butt-end section and it decreases to the top section, what is compatible with obtained results for analyzed stems.

Both wood and bark from samples with Ist degradation degree contain lower amount of lead in relation to wood and bark from samples with IInd and IIIrd degradation degree

(Fig. 10). Lead content in bark is from 5 to 6.5 times higher than in wood. Its content in bark from polluted environment (IIIrd degradation degree) is 22 % higher in relation to Ist degradation degree samples and 20 % higher in relation to IInd degradation degree samples.

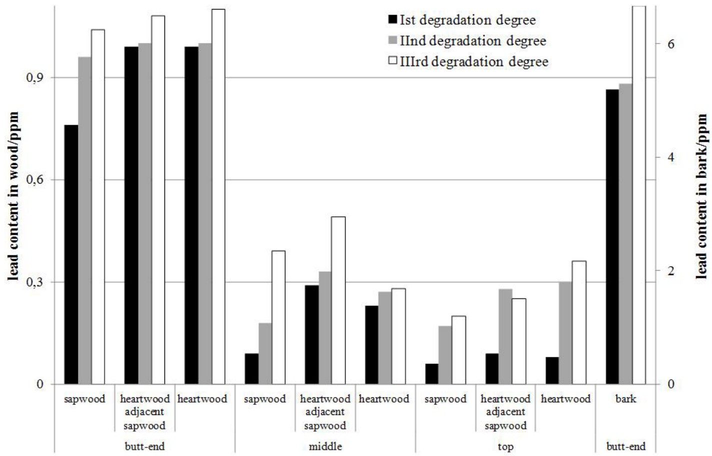

Fig. 10: Lead content in the wood and bark of analyzed pine.

Strontium content in wood is basicly higher than lead content (Krutul and Makowski 2005, You et al. 2007). Data presented in the Fig. 11 shows that strontium content both in wood and in bark is similar, regardless the environmental pollution. It is higher in bark (9.6 to 11.7 mg·kg^{-1}) and lower in wood (3.9 to 7.4 mg·kg^{-1}). Environmental pollution originated from nitrogen industrial plant causes the increase of strontium content both in wood and bark.

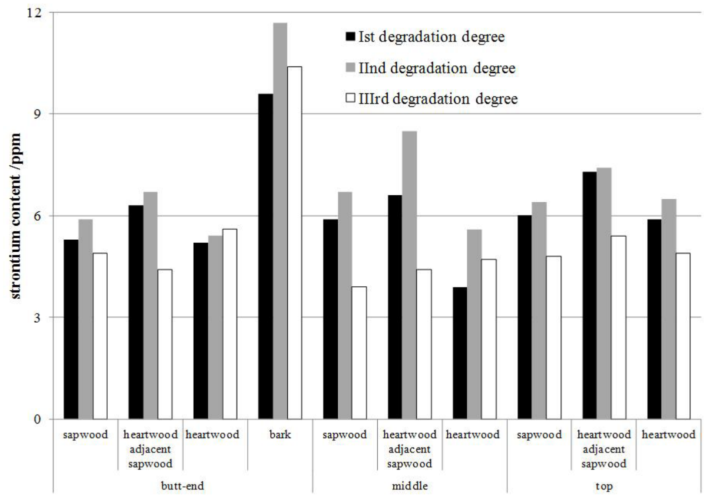

Fig. 11: Strontium content in the wood and bark of analyzed pine.

CONCLUSIONS

Irrespectively of the environmental pollution, heartwood adjacent sapwood in butt-end and middle section of the stem contains higher amount of mineral substances (or similar) in relation to sapwood, and from 20 to 40 % higher in comparison to heartwood. In top section of stems with IInd and IIIrd degradation degree sapwood and heartwood contain cca. twice lower amount of mineral substances in comparison to middle and butt-end section. Mineral substances content in bark from butt-end section is from two to seven times higher in relation to wood. Environmental pollution causes the decrease of mineral substances content in bark from butt-end section.

Calcium content in all samples is the highest in pith adjacent wood and decreases in the direction to the perimeter, regardless the stem height. Bark in butt-end section contains from two to four times higher amount of calcium in relation to heartwood and from three to seven times higher in relation to sapwood.

Nitrogen industrial plant causes the decrease of potassium content. Bark contains less potassium in comparison to wood, irrespectively of the environmental pollution.

Magnesium content is higher in the top section of analyzed stems in comparison to butt-end section. It is not dependent from the degradation degree. Bark contains from two to seven times higher amount of magnesium than wood.

Manganese content in samples with IIIrd degradation degree is 20 – 40 % higher in relation to samples with IInd and Ist degradation degree – nitrogen industrial plant causes the increase of this content both in wood and bark. It also increases iron, sodium and aluminum content in bark and decreases these contents in wood. Content of lead and strontium is increased in degraded wood both in wood and bark.

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Donata Krutul, *Tomasz Zielenkiewicz, Andrzej Radomski, Janusz Zawadzki
Andrzej Antczak, Michał Drożdżek, Tomasz Makowski
Warsaw University of Life Sciences
Department of Wood Science and Wood Protection
Nowoursynowska 159
02-776 Warsaw
Poland
Corresponding auzhor: tomasz_zielenkiewicz@sggw.pl
Phone: 0048225938642