WOOD RESEARCH
60 (4): 2015
655-662

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

Donata Krutul, Tomasz Zielenkiewicz, Janusz Zawadzki, Andrzej Radomski
Andrzej Antczak, Michał Drożdżek, Teresa Kłosińska Tomasz Makowski
Warsaw University of Life Sciences
Warsaw, Poland

(Received February 2015)

ABSTRACT

In order to specify the influence of the environmental pollution on non-metals accumulation in Scots pine trees, studies of nitrogen, sulfur, phosphorus and chlorine content were performed on samples obtained from pine stems gained from the Ist, IInd and IIIrd zone of industrial damages (tree degradation). Samples were collected from butt-end, middle and top sections of the stem in sapwood, heartwood adjacent sapwood, heartwood and in bark. Significant influence of the environmental pollution caused by nitrogen industrial plant on the nitrogen content was denoted. Nitrogen content was decreased (in relation to samples from non-polluted area) especially in sapwood and bark. Additionally, chlorine content both in wood and bark was increased.

KEYWORDS: Chlorine, nitrogen, phosphorus, Scots pine, sulfur.

INTRODUCTION

All elements necessary for plants functioning can be divided for macro-, micro- and trace elements. Conventional character of quantitative limits between macro- and microelements was the reason of the introduction of other mineral components classification, namely non-metals (N, P, S, Cl, B), alkaline metals (K, Ca, Mg, Na) and heavy metals (Fe, Cu, Mn, Mo, Zn, Ni and others). Physiological functions of these elements are very diverse, but they are essential for proper plant development (Kopcewicz and Lewak 1998). The problem of the influence of environmental pollution on particular elements content and pH changes in wood and bark was studied by (among others) Esch et al. (1996) and Hunová et al. (2014).

Nitrogen is the fourth most often found element in biomass (after carbon, oxygen and hydrogen). It is the essential element for forming of amino-acids and pyrimidine and purine bases, what means proteins, nucleotides, nucleic acids, coenzymes, chlorophyll, phytochromes, cytokines. Nitrogen participates in all biochemical reactions taking places in living organisms. That is why its deficiency is the reason of the restriction of new tissues forming. Nitrogen metabolism is strictly connected with carbon transformations because nitrogen is embodied in molecular frame. Nitric (NO_3^-) and ammonium (NH_4^+) ions are the main form of nitrogen available for plants. If plant collects nitrogen from soil, sorption properties of soil is the significant factor facilitating this process. Loamy colloids contained in soil bond NH_4^+ ions because of its positive charge, whereas NO_3^- ions are not kept in soil sorption complex and that is why they are easy available for plants. Preferential collection of nitric ions is also caused by plant metabolism – these ions regulate the activity of assimilation enzymes. Plants can not too much increase ammonium ions concentration with correspondingly higher activity of enzymes and acceleration of nitrogen assimilation, because high ammonia concentration is even toxic for them.

Sulfur is collected from the ground in the form of sulfate ions (SO_4^{2-}) or, in small amount, as sulfur dioxide from the atmosphere. It is transported through xylem and appears in many different compounds, mainly in reduced forms, in sulfhydryl groups of aminoacids, e. g. cysteine, cystine, metionine, and only in small amounts in oxidized form. Sulfur is also contained in different proteins as –SH groups or creates bridges of (–S – S –) type, what influence forming of the structure of secondary and tertiary proteins. Group –SH in cysteine takes a part in the creation of active centre of many enzymes.

The influence of nitrogen and sulfur on the enzymes activity in a boreal mixedwood forest in western Canada was studied by, among others, Hu et al. (2013). Ohmann and Grigal (1990) studied spatial and temporal patterns of sulfur and nitrogen in wood of trees across the north central United States. They stated that sulfur to nitrogen ratio increases with the sulfate deposition gradient and more sulfur is being taken up by trees than plant needs for nutrition.

Plants collect phosphorus in the form of $H_2PO_4^-$ or HPO_4^{2-} ions. It connects to many different compounds in oxidized form, creating ortho-phosphoric acid esters. It is transported both by xylem and phloem. There is always a bank of inorganic phosphorus (Pi) in plant cell, which is called metabolic. It is used in different reactions of phosphorylation and ATP synthesis. In the conditions of phosphorus deficiency this amount significantly decreases causing the decrease of ATP concentration what influences intensity of metabolic transformations. It leads to plant growth inhibition. So called pyro-phosphoric ion (PPi) is present in plant cell. It plays a role in saccharides metabolism.

Chlorine is collected by plants in the form of soluble anion Cl^- and it is transported mainly by xylem. Chlorine is essential during water decomposition in photosynthesis process. It also stimulates ATP-azis and plays a role in cells osmo-regulation. It is classified as microelement because of its low content in plants, but in other classifications it is treated as macroelement (Kopcewicz and Lewak 1998).

Excessive amount of both macroelements and microelement in plants is toxic.

Harmful action of industry significantly influences forests condition. It causes different types of damages, such as: defoliation, decoloration, growth inhibition. These damages are the base of the identification of forest stands affected by industry (Kozak et al. 1999). Forests in the area affected with industry are divided into three zones of industrial damages: Ist zone of weak damages (11-25 % of defoliation), IInd zone of mean damages (26-60 %) and IIIrd zone of strong damages (over than 60 %). They may be acknowledged as areas of, correspondingly, weak, strong, and very strong environmental pollution (Nowak et al. 2003).

The aim of this paper is to study the influence of environmental pollution originated from nitrogen industrial plant on the non-metals content in wood and bark of pine (*Pinus sylvestris* L.) depending on sample position on the cross- and longitudinal- section of a stem.

MATERIAL AND METHODS

Three cca. 70-year old stems of pine (*Pinus sylvestris* L.) were cut in december in Vth Silesia forest region. One tree was cut from the Ist zone of industrial damages (weak pollution, samples collected in the distance of 25 km from the industrial plant) one from the IInd zone (strong pollution, samples collected in the distance of 15 km from the industrial plant) and one tree from the IIIrd zone (very strong pollution, samples collected in the distance of 1 km from the industrial plant). The emission of gaseous pollutants from the nitrogen industrial plant "Kędzierzyn" included NH_3, SO_2, NO_x, H_2S, CO, hydrocarbons and others in small amounts. "Kędzierzyn" is the largest nitrogen plant in southern Poland. There is one more significant nitrogen plant in Upper Silesia (to the east from sampling area) region but it is of much lower manner. Additionally winds during whole XXth century in Poland were mainly of western direction.

Three 200 mm thick disks were cut from each stem in butt-end, half-height and top section. Samples of sapwood, heartwood adjacent sapwood and pith adjacent heartwood were collected on the cross-section using drill. Wood and bark samples were disintegrated in laboratory mill and fractioned using sieves. Dusty fraction was taken for analysis.

Content of nitrogen and other elements both in wood and bark was calculated in relation to absolutely dry samples. Content of general nitrogen was examined with Kjeldahl method and contents of elements in form of anions Cl^-, SO_4^{2-}, HPO_4^{2-} were determined using HPLC with conductometric detector.

RESULTS AND DISCUSSION

Nitrogen content in wood and bark of pine collected from three environments with different pollution degrees is presented in the Fig. 1. Regardless of the environmental pollution degree, sapwood and heartwood adjacent sapwood contain more nitrogen in comparison to heartwood.

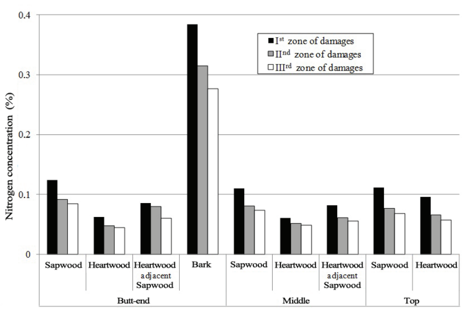

Fig. 1: Nitrogen (N) concentration in examined wood and bark.

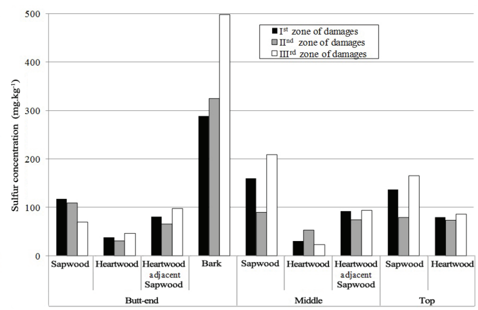

Fig. 2: Sulfur (SO_4^{2-}) concentration in examined wood and bark.

Poulson et al. (1995) examined wood of eastern hemlock (*Tsuga canadensis*) and results were similar – wood from the perimeter area contains cca. 45 % more nitrogen in relation to pith adjacent wood. Gerhart and Lauchlan (2014) stated that annual rings adjacent to pith contain cca. 0.04 % of nitrogen. Nitrogen content increases in sapwood adjacent heartwood and further in sapwood until the perimeter, where it reaches 0.20 %. According to Schulz et al. (2001) nitrogen content in bark of Scots pine samples collected from different habitats in eastern Germany varies from 3.16 to 4.12 %. Authors state that bark of Scots pine can be used as a biomonitoring tool to indicate nitrogen depositions of airborne pollutants in pine stands.

The environmental pollution causes the decrease of nitrogen content in sapwood and heartwood adjacent sapwood. Nitrogen content in these zones of wood collected from the IIIrd zone of damages is correspondingly 23 and 30 % lower in relation to samples from weakly polluted environment. Similar differences may be observed for half-height and top part of the stem. Nitrogen content in butt-end section is higher in relation to top section apart from the environmental pollution degree (correspondingly 10, 16 and 20 % higher for Ist, IInd and IIIrd zone of damages).

Bark in butt-end section contains more nitrogen in relation to other zones, apart from pollution degree. Its content is three times higher in comparison to sapwood, four times higher in comparison to heartwood adjacent sapwood and more than six times higher in relation to heartwood.

Nitrogen content in bark from the Ist zone of damages is 20 and 28 % higher in relation to, correspondingly, IInd and IIIrd zone. Nitrogen content is also higher in oak wood gained from unpolluted environment in relation to polluted one (Krutul et al. 2014). For example, nitrogen content is 45 % higher in sapwood from the butt end section, 25 % higher in the middle part and 55 % higher in the top part of the stem. Similar dependences are observed in other zones of stem cross-section.

Nitrogen content in bark is higher in comparison to wood, regardless of the environmental pollution, however differences are more significant in samples from polluted environment (Krutul et al. 2014).

Summarizing, pollution originated from nitrogen industrial plant causes the decrease of nitrogen content, both in wood and bark.

Changes in sulfur content (determined as SO_4^{2-}) in particular wood zones and sections are irregular, what is presented in the Fig. 2. Content of this element in butt-end section is the lowest in sapwood collected from the IIIrd zone of damages, when sapwood from middle and top part of the stem contains the highest amount of sulfur in wood from, correspondingly, Ist and IInd zone of damages. Sulfur content in bark increases with the degree of environmental pollution (Fig. 2). Bark from the IIIrd zone of damages contains 40 and 35 % more sulfur than, correspondingly, wood from the Ist and IInd zone of damages.

As it arises from data collected by Krutul et al. (1999), sulfur content in butt-end section sapwood from 110 year old Scots pine (polluted environment) equals 220 mg.kg^{-1}, in sapwood adjacent heartwood – 165 mg.kg^{-1} and in heartwood – 134 mg.kg^{-1}.Values obtained for samples collected in unpolluted environment are always higher. Sulfur content in bark from the stem gained from unpolluted environment (but-end section) is six times higher in relation to wood and twofold higher in comparison to bark gained from environment with very strong pollution degree and three times higher in relation to bark gained from environment with strong and weak pollution degree.

According to Esch et al. (1996), sulfur content in beech, oak and birch is correspondingly 209, 240 and 170 mg.kg^{-1}. Sulfur content (SO_4^{2-}) in analyzed pine stems reaches 200 mg.kg^{-1} in butt-end section and 170 mg.kg^{-1} in top part only in samples with IIIrd degradation degree. Sulfur content in pine wood according to Harju et al. (1997) equals 103 mg.kg^{-1}.

Environmental pollution causes the increase of sulfur content in bark from butt-end section and in sapwood from the middle and top part of the stem.

Fig. 3 presents data of phosphorus content in examined pine wood. Apart from the environmental pollution, sapwood and heartwood adjacent sapwood contain more phosphorus

(HPO_4^{2-}) than heartwood. These results are compatible with results of Krutul et al. (1999) which show the same relationship in 110 year old Scots pine. Phosphorus content in pine stems seems to be significantly dependent on the pollution degree only in butt-end section (Fig. 3).

Sapwood and heartwood adjacent sapwood from butt-end and middle section of analyzed stems from the Ist zone of damages contain more phosphorus (250 – 270 mg.kg^{-1}) than heartwood (20 – 50 mg.kg^{-1}). Additionally it may be observed that heartwood from the top section contains more phosphorus in comparison to butt-end and middle section of the stem, apart from pollution degree.

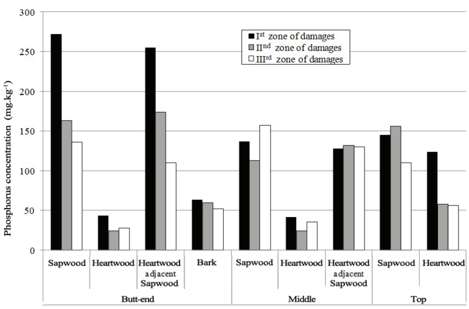

Fig. 3: Phosphorus (HPO_4^{2-}) concentration in examined wood and bark.

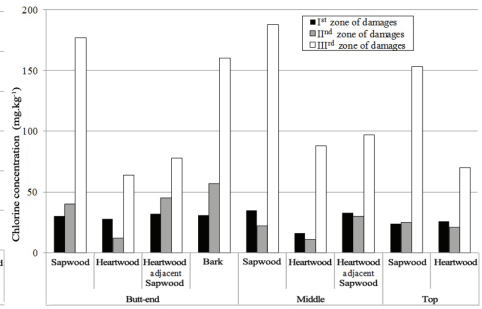

Fig. 4: Chlorine (Cl^-) concentration in examined wood and bark.

According to Krutul et al. (1999), phosphorus content in bark from 110-year old pine from unpolluted environment is three times higher in relation to polluted samples. Phosphorus content in black locust wood (*Robinia pseudoacacia* L.) according to Passialis et al. (2008), in sapwood is sevenfold higher in relation to juvenile and mature wood, obtained from different habitats (Greece, Bulgaria and Hungary). Phosphorus content in bark from trunk (breast height) is 20 to 60 % higher in relation to sapwood and cca. 15-fold higher in comparison to juvenile and mature wood.

Environmental pollution caused by nitrogen industrial plant causes the increase of chlorine content both in wood and bark. It is presented in the Fig. 4. Sapwood from stems collected in the IIIrd zone of damages, apart from stem height, contains several times higher amount of chlorine in comparison to samples gained from Ist and IInd zone of damages. The increase of chlorine content both in bark and in wood is clearly observable as a result of the pollution caused by nitrogen industrial plant.

As it arises from the data obtained by Krutul and Makowski (2005), chlorine content in sapwood from butt-end section of Norway maple gained from urban environment is several dozens times higher in relation to samples from the environment with weak and strong pollution degree and seven times higher in comparison to samples from the environment which pollution is very strong.

Esch et al. (1996) reported that in beech, oak and birch wood chlorine content equals to, correspondingly, 28, 26 and 20 mg.kg^{-1}. In analyzed wood of Scots pine (Ist and IInd degradation degree) in heartwood zone chlorine content is similar to data obtained by Esch et al. (1996). Chlorine content both in sapwood and heartwood from stems with IIIrd degradation degree is several times higher in relation to data of Esch et al. (1996).

Bark from pine stems gained from weakly and strongly polluted environment contains correspondingly five and two and a half times lower amount of chlorine in relation to samples collected from the environment with very strong pollution degree.

CONCLUSIONS

Nitrogen industrial plant which has been emitting cca.10000 tons of nitrogen oxides (NOx) and 1500 tons of ammonia a year, causes the decrease of nitrogen content in wood of Scots pine. Its content in sapwood and heartwood adjacent sapwood gained from the III_{rd} zone of damages is lower in relation to samples from II^{nd} and I^{st} zone of damages. Environmental pollution causes the decrease of nitrogen content in bark too.

Content of sulfur and chlorine is increased both in wood and bark, as a result of environmental pollution. Its content in samples from the III_{rd} zone of damages is higher in relation to samples from II^{nd} and I^{st} zone of damages.

The influence of the environmental pollution on phosphorus content, both in wood and bark, was not stated.

REFERENCES

1. Esch, M., Hofmann, D., Krebs, G., Thierfelder, C., Wünsch, R., Maier, R., Kuzel, M., Schosnig, M., Groeneveld, K.O., 1996: Elemental composition of different types of wood. Nucl. Instr. Meth. Phys. Res B 109/110: 328-331.
2. Gerhart, L.M., McLauchlan, K.K., 2014: Reconstructing terrestrial nutrient cycling using stable nitrogen isotopes in wood. Biogeochemistry 120(1-3): 1-21.
3. Harju, L., Lill, J.-O., Saarela, K.-E., Heselius, S.-J., Hernberg, F.J., Lindroos, A., 1997: Analysis of trace elements in trunk wood by thick-target PIXE using dry ashing for preconcentration. Fresenius J. Anal. Chem. 358(4): 523-528.
4. Hu, Y.-L., Jung, K., Zeng, D.-H. 2013: Nitrogen- and sulfur-deposition-altered soil microbial community functions and enzyme activities in a boreal mixed wood forest in western Canada. Can. J. For. Res. 43(9): 777-784.
5. Hunová, I., Maznová, J., Kurfürst, P., 2014: Trends in atmospheric deposition fluxes of sulphur and nitrogen in Czech forests. Environ. Pollut. 184: 668-675.
6. Kopcewicz, J., Lewak, S. (ed.) 1998: Plants physiology basics. W.N. PWN, Warsaw (in Polish).
7. Kozak, J., Troll, M., Widacki, W., 1999: Forest degradation. In: Widacki W. (ed.) Environmental changes in western Beskid caused by human impact, Geography Institute, Jagiellonian University, Cracov. Pp 33-84 (in Polish).
8. Krutul, D., Kazem-Bek, D., Sacharczuk, A., 1999: Content of some elements in bark and wood of Scots pine (*Pinus sylvestris* L.) In: 13th Scientific Conference of the Faculty of Wood Technology, Warsaw University of Life Sciences "Wood as the material of comprehensive purpose and usage" Warsaw. Pp 67-71 (in Polish).
9. Krutul, D., Makowski, T., 2005: Influence of agglomeration environment on content ofNorway maple (*Acer platanoides* L.). Annals of Warsaw Agricultural University SGGW. Forestry and Wood Technol. 56: 369-376.
10. Krutul, D., Zielenkiewicz, T., Zawadzki, J., Radomski, A., Antczak, A., Drożdżek, M., 2014: Influence of urban environment originated heavy metal pollution on the extractives and mineral substances content in bark and wood of oak (*Quercus robur* L.) Wood Research 59(1): 177-190.

11. Nowak, M., Szczepański, W., Śmigielska - Mucha, J., 2003: Main health risk of the Silesian Voivodeship forests. In: Parusel J. (ed.) Ecophysiographic description for land-use plan of the Silesian Voivodeship. Nature Heritage Centre of Upper Silesia, III 1.11. Pp 317-330 (in Polish).
12. Ohmann, L.F., Grigal, D.F., 1990: Spatial and temporal patterns of sulfur and nitrogen in wood of trees across the north central United States. Can. J. For. Res. 20(5): 508-513.
13. Passialis, C., Voulgaridis, E., Matrouka, M., 2008: Extractives, acidity, buffering capacity, ash and inorganic elements of black locust wood and bark of different clones and origin. Holz als Roh- und Werkstoff 66(6): 395-400.
14. Poulson, S.R., Chamberlain, C.P., Friedland, A.J., 1995: Nitrogen isotope variation of tree rings as a potential indicator of environmental change. Chem. Geol. 125(3): 307-315.
15. Schulz, H., Goehre, M., Hofmann, D., Jung, K., 2001. Nitrogen isotope ratios in pine bark as an indicator of N emissions from anthropogenic sources. Environ. Monit. Asses. 69(3): 283-297.

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