Annals of Warsaw University of Life Sciences – SGGW
Forestry and Wood Technology No 72, 2010: 395-400
(Ann. WULS-SGGW, For and Wood Technol. 72, 2010)

Changes in wood basic chemical composition in *Salix viminalis* in a model experiment

BOGUSŁAWA WALISZEWSKA[1], WŁODZIMIERZ PRĄDZYŃSKI[1], TAMARA CHADZINIKOLAU[2], AGNIESZKA SPEK-DŹWIGAŁA[1]

[1]Institute of Chemical Wood Technology, Poznań University of Life Sciences
[2]Department of Plant Physiology, Poznań University of Life Sciences

Abstract: *Changes in wood basic chemical composition in Salix viminalis in a model experiment.* The study analysed changes in the content of basic wood constituents of willows (*S. viminalis*) cultivated hydroponically with additives of calcium and magnesium as well as selected chemical elements. After a short period of vegetation, changes in the content of structural components in the wood of willow seedlings were observed.

Keywords: wapń, magnez, hodowla hydroponiczna, metale ciężkie, celuloza, lignina,

INTRODUCTION

From among 400 species of willows practical use has only 40. At present moment they are wide use, because an important part of investigation in range of chemistry and environmental protection became of searching a new plants characterized ability of heavy metals accumulation in their tissue at high concentration, quick increase of biomass (Szczukowski S. et al. 1997, Waliszewska and Prądzyński 2005, Smaliukas et al. 2007), what can be used like an energetic material as well as in wood industry (Szczukowski S. et al. 1998, Mirck et al. 2005). What more it is used like an indicator of pollution (Mertens et al. 2004) and like a buffer zones can limit a superficial raftings from field to waste waters preventing their eutrophication or like a protective willow zone round roads and highways limited the air pollution and protect field before contamination (Faliński, 1990). In recent years, application of the *Salix* genus has been expanded considerably. Willow effectiveness in the reclamation of degraded industrial land (Wróblewska et al., 2004) as well as in sewage treatment (Waliszewska et al. 1999, 2004) is well recognised. Bush varieties of willow, in particular *Salix viminalis*, employed in environmental protection are known for their ease of adaptation to new environmental conditions (Hermle et al., 2006). The willows root system is capable to taking not only nutritious substances but also can bond of harmful substances, in this the heavy metals contained in sewages, the settlings as well as in the soil. Heavy metals presented in natural environment are essential for plants but at higher concentration are toxic, like cooper (Cu), zinc (Zn), nickel (Ni) (Lee et al. 2004).

Contamination by heavy metals in the natural environment is a major problem for human health, crop cultivation and quality of environment. What more behavior of heavy metals is various in contaminated soil (Mleczek et al. 2009) and their affected the uptake by plant are controlled by soil pH value, redox condition, organic matter (Lee *et* al. 2004), low molecular weight organic acids speciation of metals (Dai *et* al 2004) and probably by the presented in environment amount of macroelements, first of all calcium and magnesium ratio (Ca/Mg).

Different species of willows growing in different conditions show an essential differences in chemical composition of wood, like contents of cellulose, holocellulose and lignin, as well as in accumulation of heavy metals. (Waliszewska and Prądzyński 2001).

Therefore essential is to study how above-mentioned factors influence on chemical parameters of wood.

The aim of presented study was the qualification of changes in structure and chemical composition of willows seedlings exposed on cadmium, cooper, lead and zinc in dependence of Ca/Mg ratio.

MATERIALS AND METHOD

One year old *Salix viminalis* cuttings came from a 2-year old rootstock harvested in the end of November and stored in moisture box at 5 ºC. Before experiment the standardized stocks (20 cm of length and similar diameter: diameter of shoots – 6-8 mm, diameter of pith – 3.8-4.0 mm) were incubated for 10 days for rooting in 50% concentration of Knop medium (10 cm^3 of 10% $Ca(NO_3)_2$, 2.5 cm^3 of 10% KNO_3, 1.2 cm^3 of 10% KCl, 10 cm^3 of 2.5% KH_2PO_4, 5 cm^3 of 5% $MgSO_4$ and 0.25 cm^3 of 0,25% $FeCl_3$ in 1 dm^3 of acidified water at pH=3.94). After that cuttings were put individually into hydroponic pots and stabilized by the ultra pure river sand. Experiment was conducted 21 days and the reference systems was combination without heavy metals in Knops medium. Four solution with different Ca/Mg ratio were used as follows: 20:1, 4:1, 1:$^1/_4$ and 1:10. The each plant was incubated in 0.5 dm^3 of 0.1 mM solution of each of tested 4 heavy metals (control) and in four experimental combinations where one of metals was at 0.5 mM concentration while other accompanied at 0.1 mM for example: $Cd_{0.5}$, $Cu_{0.5}$, $Pb_{0.5}$, $Zn_{0.5}$ (Table 1). Solution of individual heavy metals (Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}) was prepared on the base of analytical grade nitrates (V) dissolved in de-ionized water (Milli-Q) acidified to 0.08% nitric acid content (Ultrapure).

Table 1. Scheme of different sets of the heavy metals concentrations (mM) in the experiment

	Ca/Mg ratios			
$Cd_{0.5}$	0.5	0.1	0.1	0.1
$Cu_{0.5}$	0.1	0.5	0.1	0.1
$Pb_{0.5}$	0.1	0.1	0.5	0.1
$Zn_{0.5}$	0.1	0.1	0.1	0.5

The experiment was performed in a controlled climate chamber equipped with fluorescent lamp (MASTER TL-D Secura 58W/830 1SL) providing a photon (radiation) flux of 220 µE sec^{-1} m^{-2} (µmol sec^{-1} m^{-2}) in the top of the plant for 16 hours of 20±1°C and humidity of 81-84%. Loss of water was compensated by pure water. The growth medium was not replaced during experiment with metals and no bactericide was used.

Samples of willow stems used for the determination of chemical composition were seasoned in an air-conditioned facility until they reached air-dry state. Once they reached the required moisture content, they were comminuted together with bark using a laboratory mill Pulverisette 15 of Fritsch Company and an analytic fraction of 0.5-1.0 mm was separated. The material for cellulose and lignin assays was deprived of extractive substances. Investigations of the chemical composition were conducted according to the PN 92/P-50092 standard.

RESULTS

Table 2. Content of selected chemical composition of *Salix* in relation to Ca/Mg ratio and heavy metals amount in solutions

Kind of metal	Cellulose [%]	Lignin [%]	Extractable substances [%]
0	41.06	23.26	3.72
	4:1 Ca/Mg ratio		
$Cd_{0.5}$	41.50	24.51	3.51
$Cu_{0.5}$	41.14	23.40	2.39
$Pb_{0.5}$	43.54	24.46	3.00
$Zn_{0.5}$	43.11	24.40	4.09
	20:1 Ca/Mg ratio		
$Cd_{0.5}$	45.72	26.85	2.87
$Cu_{0.5}$	44.11	23.72	6.39
$Pb_{0.5}$	39.75	23.32	4.42
$Zn_{0.5}$	43.92	22.49	4.15
	$1:^1/_4$ Ca/Mg ratio		
$Cd_{0.5}$	44.85	22.76	3.65
$Cu_{0.5}$	43.78	22.61	3.63
$Pb_{0.5}$	44.88	23.26	3.95
$Zn_{0.5}$	44.14	23.53	4.17
	1:10 Ca/Mg ratio		
$Cd_{0.5}$	43.51	22.89	2.61
$Cu_{0.5}$	46.81	23.52	4.78
$Pb_{0.5}$	43.78	23.10	3.03
$Zn_{0.5}$	44.93	23.11	3.96

The analysis of the cellulose content in willow seedlings incubated in individual systems of different Ca/Mg ratios revealed variability of its content depending on the presence of the metal which occurred at the concentration of 0.5 mM (Table 2).

With regard to individual metals and taking into consideration initial cellulose contents in seedling, these relations were as follows:

$Cd_{0.5}$: 20:1 > $1:^1/_4$ > 1:10 > 4:1,
$Cu_{0.5}$: 1:10 > 20:1 > $1:^1/_4$ > 4:1,
$Pb_{0.5}$: $1:^1/_4$ > 1:10 > 4:1 > 20:1,
$Zn_{0.5}$: 1:10 > $1:^1/_4$ > 20:1 > 4:1.

The greatest changes in the cellulose content were determined in plants incubated in combinations: $Cu_{0.5}$ (1:10 Ca/Mg) and it was 5.75%. A drop in cellulose content was observed only for seedlings incubated in the $Pb_{0.5}$ (20:1 Ca/Mg) combination. It is difficult, on the basis of the obtained research results, to point unequivocally to simple correlations between the Ca/Mg ratio and the direction of changes in the cellulose content. Series of Ca/Mg relationships for individual metals with regard to changes in cellulose content fail to indicate that the Ca/Mg ratio influenced the amount of this biopolymer in any significant way. Nevertheless, differences between cellulose content and the metal present in the solution appear to point to a greater role of the ions of heavy metals found in the solution than that of both macroelements, i.e. Ca and Mg.

The higher the content of cellulose and the lower that of lignin, the greater is the possibility of utilisation of wood as raw material. That is why, the examined seedlings were also subjected to analysis for lignin content and the obtained results are presented in Table 2. Taking into consideration the concentration of the incrusting substance before the beginning of the experiment, changes in its quantities in incubated plants in the presence of individual metals can be shown in the form of declining series:

$Cd_{0.5}$: 20:1 > 4:1 > 1:10 > 1:1/4,
$Cu_{0.5}$: 20:1 > 1:10 > 4:1> 1:$^{1}/_{4}$,
$Pb_{0.5}$: 4:1 > 20:1 > 1:$^{1}/_{4}$ > 1:10,
$Zn_{0.5}$: 4:1 > 1:$^{1}/_{4}$ > 1:10 > 20:1.

Similarly to the case with cellulose, the obtained results indicate variations in lignin content depending on the metal occurring at the concentration of 0.5 mM. From practical point of view, the most important are drops in lignin concentrations which were the biggest in plants incubated in combinations: $Zn_{0.5}$ (20:1 Ca/Mg) and $Cu_{0.5}$ (1:$^{1}/_{4}$ Ca/Mg) and which amounted to: 0.77% and 0.65%, respectively. However, such changes in lignin content in seedling cannot be considered as significant.

Bearing in mind the earlier results regarding cellulose, it should be said that plants in which the greatest changes in cellulose content took place were characterised by changes in lignin quantities, from 0.4% to 0.5%. This indicates possibility of selecting those combinations with the aim to explain changes in cellulose and lignin contents in incubated willow shoots.

The analysis of the extractive substances content revealed their considerable changes in the incubated shoots depending on the Ca/Mg ratio in treatments containing different heavy metals. Changes in the content of extracted substances were from 2.39% to 6.39%, Changes in the content of extractive substances ranged from 2.38% to 6.39% which can indicate dynamic physiological processes taking place during the experiment, and can be described using the following dependencies:

$Cd_{0.5}$: 1:1/4 > 4:1 > 20:1 > 1:10,
$Cu_{0.5}$: 20:1 > 1:10 > 1:$^{1}/_{4}$ > 4:1,
$Pb_{0.5}$: 20:1 > 1:1/4 > 1:10 > 4:1,
$Zn_{0.5}$: 1:1/4 > 20:1 > 4:1 > 1:10.

The highest increase in the amount of extracted substances was found in the case of seedlings incubated in combinations $Cu_{0.5}$ (Ca/Mg 20:1) and $Cu_{0.5}$ (1:10 Ca/Mg) whose quantities amounted to: 6.39 % and 4.78%, respectively (Table 2). On the other hand, the greatest drops were observed in combinations: $Cu_{0.5}$ (Ca/Mg 4:1) and $Cd_{0.5}$ (Ca/Mg 1:10) where the respective quantities were: 2.39% and 2.61 %.

The reported changes in the wood chemical composition of willow (*Salix viminalis*) seedlings incubated in a model experiment could be attributed to the action of heavy metals present in the medium. However, no clear correlation was found between the varying Ca/Mg ratio and supplementation with individual chemical elements and changes in wood basic constituents. Depending on the Ca/Mg coefficient, the presence of heavy metals can either increase or decrease quantities of substances soluble in organic solvents but further special model investigations are required to confirm this hypothesis.

Acknowledgements

The experimental part of this study was supported by the Ministry of Science and Higher Education (State Committee for Scientific Research KBN), Grant No. N N310 3218 33.

REFERENCES

1. DAI J., BECQUER T., ROUILLER J. H., REVERSAT G., BERNHARD-REVERSAT F., LAVELLE P., 2004 : Influence of heavy metals on C and N mineralization and microbial biomass in Zn-, Pb-, Cu-, and Cd-contaminated soils. Applied Soil Ecology 25, 99–109.
2. FALIŃSKI J.B., 1990: Zarys ekologii. Wierzby. PWN, Warszawa-Poznań.
   HERMLE S., GÜNTHARDT-GOERG M. S., SCHULIN R., 2006: Effects of metal-contaminated soil on the performance of young trees growing in model ecosystems under field conditions. Environ. Pollut. 144, 703-714.
3. LEE T.M., LAI H.Y., CHEN Z.S., 2004. Effect of chemical amendments on the concentration of cadmium and lead in long-term contaminated soils. Chemosphere 57, 1459–1471.
4. MERTENS, J., VERVAEKE, P., SCHRIJVER, A.D., LUYSSAERT, S., 2004: Metal uptake by young trees from dredged brackish sediment: limitations and possibilities for phytoextraction and phytostabilisation. Sci. Total Environ. 326, 209–215.
5. MIRCK J, ISEBRANDS JG, VERWIJST T, LEDIN S., 2005 : Development of short-rotation willow coppice systems for environmental purposes in Sweden. Biomass and Bioenergy, 28, 219-228.
6. MLECZEK M., MAGDZIAK Z., RISSMANN I., GOLINSKI P., 2009: Effect of different soil conditions on selected heavy metals accumulation by *Salix viminalis* tissues. Journal of Environmental Science and Health, Part A, 44.
7. SMALIUKAS, D., NOREIKA, R., KARALIUS, D., 2007: Clonal selection of *Salix* L. taxa perspective for biofuel production, evaluation of their dendrometric characteristics and accumulation of biomass in short rotation plantations. Biology 53, 59–62.
8. SZCZUKOWSKI S., TWORKOWSKI J., WIWART M., PRZYBOROWSKI J., 1997: Wiklina (Salix sp.). Uprawa i możliwości wykorzystania. Wyd. ATR Olsztyn.
9. SZCZUKOWSKI S., TWORKOWSKI J., KWIATKOWSKI J., 1998: Możliwości wykorzystania biomasy Salix sp. pozyskanej z gruntów ornych jako ekologicznego paliwa oraz surowca do produkcji celulozy i płyt wiórowych. Postępy Nauk Rolniczych 2: 53-63.
10. WALISZEWSKA B., PODOBIŃSKI A., BOBKIEWICZ K., 1999: Skład chemiczny wierzb i redukcja metali ciężkich w hydrobotanicznych oczyszczalniach wód. Mat. Konf. Nauk. WTD SGGW, W-wa, s. 59-65, tab. 5, ryc. 5, poz. lit. 7.
11. WALISZEWSKA B., PRĄDZYŃSKI W. (2001): Podstawowy skład chemiczny i stopień polimeryzacji celulozy w jednorocznych i wieloletnich wierzbach krzewiastych rosnących przy autostradzie A-2. Mat. IV Krajowe Sympozjum pt. „Reakcje biologiczne drzew na zanieczyszczenia przemysłowe", ss.10, tab. 2, ryc. 3, poz. lit. 27.
12. WALISZEWSKA B., PRĄDZYŃSKI W., ZBOROWSKA M., PEREK T., 2004: Chemical composition and heavy metals content in willows growing in hydrobotanic waster treatment plants. In.: Selected Processes at the Wood Processing. (Eds. V. Velkova, A. Geffert, F. Kacik) Bobrownik 2004.
13. WALISZEWSKA B., PRĄDZYŃSKI W., 2005: Chemical composition and heavy metals content in willow trees (*Salix caprea L.*), Ann. Warsaw Agricult. Univ.- SGGW, Forestry and Wood Technology, No 56.
14. WRÓBLEWSKA H., WALISZEWSKA B., PRĄDZYŃSKI W., CZAJKA M., MAĆKOWIAK K., 2004: Investigations of S*alix purpurea* L. plantation on soils supplied with compost from wood wastes. In.: Selected Processes at the Wood Processing. (Eds. V. Velkova, A. Geffert, F. Kacik) Bobrownik 2004, tab. 3, ryc. 5, poz. lit. 2.

Streszczenie: *Zmiany w podstawowym składzie chemicznym drewna sadzonek Salix viminalis w modelowym doświadczeniu.* W pracy zbadano zmiany w zawartości podstawowych składników drewna wierzby *S. viminals* pod wpływem hydroponicznej uprawy z dodatkiem wapnia i magnezu oraz wybranych pierwiastków. Po krótkim okresie wegetacji zaobserwowano zmiany zawartości składników strukturalnych w drewnie sadzonek wierzbowych.

Corresponding authors:

Bogusława Waliszewska, Włodzimierz Prądzyński, Agnieszka Spek-Dźwigała
Poznań University of Life Sciences
Institute of Chemical Wood Technology,
Ul. Wojska Polskiego 28
60-637 Poznań
e-mail: bwaliszewska@up.poznan.pl
e-mail : wpradzynski@up.poznan.pl
e-mail : adzwigala@up.poznan.pl

Tamara Chadzinikolau
Poznań University of Life Sciences
Department of Plant Physiology,
Ul. Wojska Polskiego 28
60-637 Poznań
e-mail: tamaris@up.poznan.pl