### Heavy Metals Accumulation in Wood Tissue of the Main Forest Forming Species in Northern Steppe of Ukraine

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#### **Abstract**

The content of heavy metal (Cd, Pb, Cu, Zn, Ni, Mn) in wood of Scots pine (*Pinus sylvestris* L.) and black locust (*Robinia pseudoacacia* L.) within the Northern Steppe of Ukraine was analyzed. A species specificity of heavy metal accumulation and dependence of their concentration on age of investigated wood breeds have been identified.

Key words: Northern Steppe, Scots pine, black locust, heavy metal accumulation.

#### Аннотация

Проанализировано содержание тяжелых металлов (Cd, Pb, Cu, Zn, Ni, Mn) в древесине сосны обыкновенной (*Pinus sylvestris* L.) и робинии ложноакации (*Robinia pseudoacacia* L.) в лесных насаждениях Северной Степи Украины. Установлены видоспецифичность накопления тяжелых металлов и зависимость их концентраций от возраста древесины исследованных пород.

**Ключевые слова:** Северная Степь Украины, сосна обыкновенная, робиния ложноакация, тяжелые металлы.

#### Introduction

The challenge of heavy metal compartmentation in autotrophic block of forest ecosystems is crucial in the study of toxic effects and plant resistance mechanisms (Moral, 1994; Prasad, 1999, 2001).

Study of heavy metal bioaccumulation in different types of plant communities is of considerable interest. In fact, plants play an important role in chemical elements redistribution between the individual components of biosphere, as autotrophic unit of ecosystem. Forest ecosystems have particular significance in such process as a dominant geochemical regulator of heavy metal cyclic mass flow on the global level (Kandler and Innes, 1995; Kabata-Pendias and Pendias, 2001).

Out of all proportion to the natural concentrations, excessive concentrations of heavy metals in the environment can greatly affect on plant organism functioning, reduce forest biotic productivity, deteriorate their recreational potential, and change the wood quality characteristics (Cheng et al, 1994; Appenroth, 2010; Tyler et al, 1989; Hansch and Mendel, 2009; Thapa et al, 2012; Shahid et al, 2014). It can eventually compromise the wood ecological safety (Prasad and Hagemeyer, 1999; Folkeson, 1983).

It is actual and timely investigation of forest stands role in the processes of heavy metal migration and deposition within forest biocenoses, especially at sites of anthropogenic impact. Solution of such challenge will allow to find the mechanisms of forest-forming species selective ability to absorb and accumulate heavy metals into their tissues and remove them from biogeochemical cycle for a long time. Excessive concentrations of heavy metals cause deleterious effects on plant physiological processes in varying degree, thereby it changes the integral indicator of woody plant functioning (phytomass). According to literature reports, woody plants answer to environmental pollution with reducing their biotic productivity (Ross, 1994; Prasad, 2001).

Modern domestic scientific literature contains no systematic research regarding heavy metal accumulation in wood of forest-forming species in man-made areas (Schröder et al, 2009; Febrianto et al, 2009).

Territory of Northern Steppe in Ukraine is affected by significant anthropogenic impact. The regional forest ecosystems can be considered as potential concentrators of pollutants caused by with different technogenic impact. The study of ability of forest wood to accumulate heavy metals is particularly topical because accumulated toxins are eliminated from biogeochemical cycle in forest ecosystem for a long time (Balsberg Pahlsson, 1989; Itoh et al, 2006; Khokhotva, 2010; Lepp, 1975; Boyd, 1998; Risto et al, 2005; Marko-WorłOwska et al, 2011).

The study goal was to determine the accumulation properties of forest-forming species (Scots pine and black locust) of different age groups in relation to heavy metals.

Scots pine (*Pinus sylvestris*) and black locust (*Robinia pseudoacacia*) species were studied. Scots pine is fast-growing, photophilous, wind-firm and drought-resistant tree species. The growing man-made stress in terms of urban ecosystems showed increased sensitivity of this species to pollution (Baumann et al, 2006; Kuznetsova et al, 2010). Pine is one of the first which shows the signs of degradation and dies in zones of adverse ecological environment. That is why this type is recommended for use in biomonitoring (Pöykiö et al, 2010; Risto et al., 2005).

Black locust is native to the United States, though the extent of its original range is not accurately known (Ford et al, 2006; Roach, 1980). Black locust has been planted in many temperate climates and is naturalized throughout the United States, within and outside of its historical range, and in some parts of Europe. Black locust inhabits a broad range of forest types and conditions within its native range, though it develops and grows best in the cove or mixed-mesophytic forests of the central and southern region (Malcolm et al, 2008; Rice et al, 2004).

Scots pine and black locust are the main forest-forming species of natural and artificial forests within Northern Steppe, and they can be seen as transformers of the heavy metals cycle and selective concentrators of toxic elements, under the conditions of their excessive concentrations in the environment (Marko-WorłOwska, 2011).

### Methodics of the research

The survey area is located within the urban forests of Northern Steppe of Ukraine. This forest performs the recreational and phytomining functions. Studies of location include mitigation of technogenic load caused by intensive development of the steel industry, mining, traffic activity.

The priority pollutants of the region emissions of these enterprises are presented as such heavy metals as Cd, Pb, Cu, Zn, Ni, Mn (Ecological passport of the Dnipropetrovsk region, http://www.menr.gov.ua/docs/protection1/dnipropetrovska/Dnipropetrovska\_ekopasport\_2013.pdf).

The trees of Scots pine and black locust (in the locations of urban forest) of different age groups such as: young-age group (I-st and II-nd class) - 1-st, 2-nd locations, middle-age group - 3-d location; mature (4-th location) and overmature (5-th location) group, were collected. The plants are located in sample areas of urban forest at the following coordinates: 1-N 48 28.182 E 34 49.721; 2-N 48 31.2830 E 34 51.321; 3-N 48 31.239 E 34 50.091; 4-N 48 32.123 E 34 49.594; 5-N 48 20.316 E 35.10.026

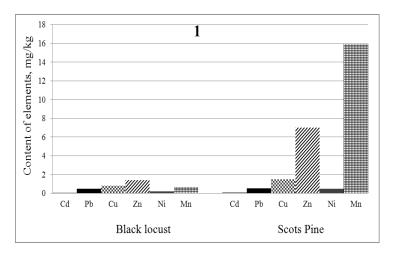
The sample areas of the size of  $25 \times 25$  m were established in an area of urban forests. On the plot, the recount of trees with the measuring of their diameters was done. Then the five model trees of the same diameter were chosen. The saw cut was made on every original that allowed to determine the age of a tree by calculation of annual rings of wood. The trees of the same age with stud block wood of trunk at a height of 1.3 m in size 5-6 cm in height, were selected. Stud block was exempted from the bark. Wood (tissue) was fragmented by an electric saw to kerf waste fraction of 1-1.5 mm. Average sample was prepared by mixing five individual samples. The sample

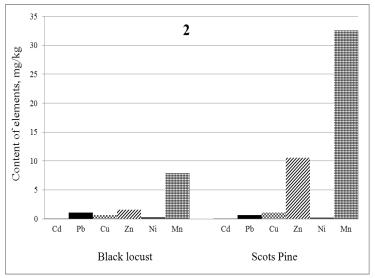
for the study was 5 g. The weighed sample was burned in a muffle furnace UF - 1207 at 1200°C with an accuracy of temperature maintenance  $\pm$  10°C.

In the obtained samples, the total number of mobile forms of metals in the soil was determined using acid extraction. 1M HNO3 and acetate-ammonia buffer solution (pH 4,8) were used to extract heavy metals to determine their mobile forms. Heavy metals (Pb, Cd, Ni, Zn, Cu, Mn) in the wood samples were determined by atomic-absorption method in the air-acetylene flame using spectrophotometer C 115 M1 with the help of software. The assay was performed in triplicate, the data were processed using standard statistical methods. Element content was calculated in mg / kg of air-dry substance.

#### Results and discussion

According to the results of heavy metal concentration study in wood tissues, there were found a significant differences in deposit ability between both the studied species and different age groups (Fig. 1, 2).





**Fig. 1.** Heavy metal concentration in wood of black locust and Scots pine on the localities 1 and 2 within the recreational forests

Cd concentrations in different age groups of black locust wood were within range 0.01 to 0,15 mg/kg. There was set the correlation between Cd concentration and tree age: 3-year-old wood

contained 0.01 mg/kg, 12-year-old 0,03 mg/kg, and 45-year-old 0,15 mg/kg, which was 14 times higher than Cd concentration in 3-year-old wood.

Cadmium is particularly toxic element that is not among the essential plant elements but it is effectively absorbed by plant root system (Hagemeyer and Schafer, 1995; Bunluesin et al, 2007; Das and Samantaray, 1997). Entry of such element into plant organism is increased with rise of its concentration in soil. According to Kabata-Pendias and Pendias (2001), cadmium transport into the plant organism occurs by carrying agent similar to zinc, but it is limited due to the fact that it easily takes up most of the exchange positions in the active substances of cell walls. Other researchers have shown that cadmium is transported to the overground part in cationic form, as it is represented in the form of Cd<sup>2+</sup> ion in the intercellular fluids of the root and leaf tissues (Moral et al, 1994; Ross, 1994). It is noted that a rapid redistribution of this metal to other vegetative organs occurs through phloem under condition of cadmium entry into plant organism through the leaves (Iretskaya, 1998; Zhang and Song, 2005; Gaudet et al, 2011; Shin et al, 2007; Shah, 2011).

Black locust and Scots pine have shown maximal cadmium accumulation in wood of the oldest tree. The wood of overmature samples contained 0.11 mg/kg, and the youngest one had a minimal concentration of 0.04 mg/kg. Relative to the absolute values of cadmium concentration, in the wood of black locust it was higher than in the common pine wood tissue.

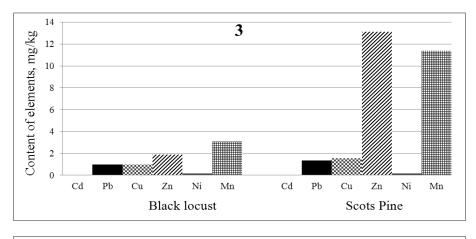
In the youngest age group, there was registered the lowest level of cadmium, when in the wood tissue of both species there was recorded the highest value of zinc concentration.

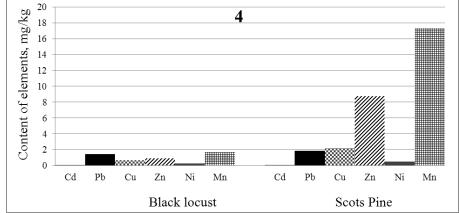
Thus, the results of the analysis confirm the hypothesis regarding cadmium and zinc antagonistic interactions (Kandler and Innes, 1995). The rate of zinc entry into plant organism is influenced by many factors. Zinc acts as cadmium antagonist in case of cadmium compounds presence as a part of polyelemental entry in the environment (Kandler and Innes, 1995; Hambidge et al, 2010). Concerning cadmium and zinc interaction, there is evidence for both antagonism and synergism between these elements in the processes of their absorption and transport (Bunluesin, 2007, Zhang et al, 2005).

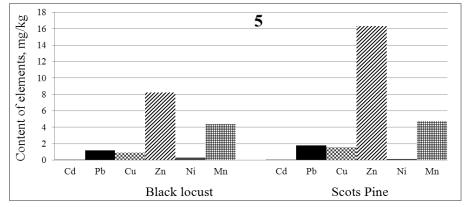
Number of studies has shown that plants can absorb lead from both soil and air, despite lead is considered as a metal with low biological availability and accumulated in roots (Jarvis et al., 1976; Isermann, 1977; Lin, 2000). The soil pH values do not effect on lead translocation processes, because Pb is capable of forming covalent bonds regardless of pH values (Jiang, 2000). Lead translocation from roots to overground parts of plant is sufficiently limited, and only about 3% of toxicant quantity entry to the stem (Jiang, 2000, Kabata-Pendias, 2001). It is proposed the hypothesis for lead is not absorbed directly by the roots from soil but sorbed from plant residual material that has accumulated near them (Lin, 2000).

Our research found that the range of Pb was more widespread concentration in the both studied species and amounted 0.47 to 1.46 mg/kg (black locust) and 0.54 to 1.83 mg/kg (Scots pine). Correlation between Pb concentration and tree age was not identified. The highest concentration of lead was indicated in the black locust (1.46 mg/kg), and in Scots pine (1.83 mg/kg) of the same age of 45. The minimal concentration of this metal was registered for overmature trees of both species.

From the data obtained on cuprum concentration it was revealed that indexes variation for black locust trees in all the studied age groups do not exceed 0.33 mg/kg. The highest concentration of this metal was fixed for black locust trees of 12 years old. Actual content and range of copper concentrations in Scots pine wood were higher compared to black locust. For this species, it can be explained by the fact that common pine is considered to be the copper concentrator (Grishko et al., 2012).







**Fig. 2.** Heavy metal concentration in wood of black locust and Scots pine on the localities 3–5 within the recreational forests

According to the literature data, accumulation index of this metal in pine needles was 3.35 to 5.97. Concentration of copper in the wood of pubescent oak was 1.80 mg/kg, which was higher than that in black locust, and much less compared to Scots pine.

The processes of nickel absorption from soil and its transport into plants are underrecognized. Soluble forms of nickel are absorbed actively by plant roots, where absorption of this element significantly correlates with its concentration in the cultivation medium (Bergkvist et al, 1989; Costa, 1998; Denys et al, 2002; De Varennes et al, 1996).

The results of our studies showed that the actual nickel concentration in the both studied species is quite low. The range of values for black locust 0.159 to 0.30 mg/kg, and Scots pine 0.15 to 0.48 mg/kg. The lowest concentration of this metal was recorded in the wood of both black locust and Scots pine at the age of 12 years old. Maximal accumulation of Ni was defined in Scots pine trees of 45 years old, and in young black locust trees of 3 years old. So, according to the presented

data, correlation in accumulation between nickel concentration and tree age has not been established.

As for all studied areas, absolute amount of manganese was the highest in both black locust and Scots pine species, compared to another metals. Value range of manganese concentration varied from 0.65 to 7.94 mg/kg in black locust, and in Scots pine - from 4.78 to 32.56 mg/kg. As for Scots pine, the maximum concentration of the metal is observed in samples of plants of 31 years old. The second position of the accumulation of manganese is fixed in mature plants. Average amount of metal is set in oldest plants and finally the least –in the young-age groups. Similar regularities of concentration Mn in plants of different ages fixed for black locust. The results show predominance of manganese concentration four times in Scots pine compared to black locust, by the maximum index in the trees of studied species at middle-aged group.

#### **Conclusions**

It was found that wood tissue of Scots pine and black locust accumulated cadmium in high concentrations in both species according to the age.

Indexes of zinc accumulation in the wood of Scots pine exceeded the maximal value in the wood tissue of black locust. The results of our research demonstrated antagonistic interaction of cadmium and zinc.

The highest copper concentrations were found in the trees of the age of 45. Lead was identified in all wood samples of all ages. Maximum of accumulation happened in the oldest samples. The trend of increase concentration of metal for both species was not found.

As for nickel there was established the opposite tendency for both studied species. If in black locust maximum accumulation of nickel was fixed in the youngest samples, then in Scots pine – in samples of 45 years old.

It was not found the mangan content in both studied species depending on the age. The absolute value of the amount of mangan in Scots pine is much higher compared to black locust.

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# Накопления тяжелых металлов в древесине основных лесообразующих видов деревьев в Северной Степи Украины

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#### Резюме

Сосна обыкновенная и робиния ложноакация — основные лесообразующие виды искусственных лесов Северной Степи Украины. Эти породы можно рассматривать в качестве трансформаторов круговорота тяжелых металлов и селективных концентраторов токсичных концентраций данных элементов. Цель данного исследования заключалась в определении способности депонирования тяжелых металлов древесиной сосны обыкновенной и робинии ложноакации разных возрастных групп.

Установлено, что концентрация Кадмия в разных возрастных группах деревьев робинии ложноакации находилась в пределах от 0.01 до 0.15 мг/кг. Для сосны показано максимальное накопление Кадмия в древесине деревьев старшей возрастной группы. В молодом возрасте для древесных пород зарегистрирован наиболее низкий уровень содержания Кадмия, когда как для другого исследуемого металла — Цинка — для молодняка определены самые высокие его концентрации в тканях обоих древесных видов.

Диапазон концентрации Плюмбума намного шире для обоих изученных видов, который составил 0.47—1.46 мг/кг (робиния ложноакация) и 0.54—1.83 мг/кг (сосна обыкновенная). Корреляции между концентрированием Плюмбума и возрастом деревьев не обнаружено. Самая высокая концентрация данного элемента выявлена в древесине как робинии ложноакации, так и сосны обыкновенной в возрасте 45 лет; минимальная концентрация зарегистрирована для деревьев обоих видов переспелой возрастной группы.

Выявлено, что концентрация Купрума для робинии ложноакации во всех изученных возрастных группах не превышает 0.33 мг/кг. Фактическое содержание и диапазон концентраций Купрума в древесине сосны обыкновенной были выше, по сравнению с робинией ложноакацией. Фактическая концентрация Никеля в обоих исследованных видах довольно низкая. Максимальное накопление указанного металла установлено для деревьев сосны 45 лет и для 3-летних экземпляров робинии ложноакации.

Содержание Марганца было самым высоким как для робинии ложноакации, так и для сосны обыкновенной, сравнительно с другими исследованными металлами. Диапазон концентрации Марганца составлял 0.65–7.94 мг/кг для робинии ложноакации и 4.78–32.56 мг/кг для сосны обыкновенной. Результаты показывают превышение Марганца в четыре раза в древесине сосны, по сравнению с робинией.