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DYNAMICS OF CHLORINE CONTENT IN LEAVES OF WOODY PLANTS OF PROTECTION FOREST BANDS IN THE CITY OF ZAPORIZHZHYA

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Abstract

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As a result of the activity of industrial enterprises, atmospheric air is being contaminated by gaseous pollutants. Such substances as chlorine and hydrogen chloride are considered to be harmful for both humans and plants. Vegetation is a universal filter that is able to combat the environmental pollution by industrial emissions with the help of appropriate technical facilities. The aim of this study is to analyze the level of accumulation of chlorine in the leaves of woody plants that grow in the area of forest plantations of sanitary protection zones of industrial enterprises. The objects of the study were the species of woody plants in the area of protective plantations of a number of enterprises in Zaporizhzhya: ZTMC, ZALK, ZABR, Zaporizhstal, Zaporizhzhya Ferroalloy Plant, Zaporizhvohnetryv, Ukrgrafit and Zaporizhtransformator. We established that during the vegetation period, a gradual accumulation of the element was the most intense in mature leaves, whose growth had already ceased. The maximum amount of chlorine was found at the end of the vegetation period. The concentration of the pollutant in leaves of woody plants in the area of sanitary protection zones of industrial enterprises is linearly proportional to the level of emissions of the pollutant into the atmosphere by a given enterprise. The largest coefficient of relative accumulation of chlorine in the leaves of such plants as *Catalpa bignonioides, Acer negundo, Robinia pseudoacacia*, *Juglans regia, Populus alba*, which can be used as information sites for the purpose of bioindication of atmospheric air pollution with chlorides, was established.

Key words: sanitary protection zones, green plantations, accumulation, chlorides, leaves.

Introduction

Zaporizhzhya is a large industrial center. In terms of air pollution, which is estimated to be at 7.8 points according to the scale of pollution and 2.3 according to the pollution index, Zaporizhzhya occupies the 10th place in Ukraine.

The ingredients of industrial emissions, such as chlorine and hydrogen chloride, are harmful for both humans and plants. Pollution of atmospheric air occurs during the work of titanium-magnesium combines (Eydenzon, 1964), galvanic workshops, enterprises producing hydrochloric acid, organic dyes, plastics, cement, superphosphate, and lime (Manning, Feder, 1985; Artamanov, 1986), factories that produce detergents, soda, insecticides, hydrochloric and acetic acid (Influence of pollution on vegetation, 1981). Hydrogen chloride is detected in exhaust gas of vehicles and gets into the environment during the burning of plastic waste that contains PVC particles (Influence of pollution on vegetation, 1981). Atmospheric air pollution by this substance in the area of metallurgical enterprises is observed as a result of the use of hydrochloric acid during melting, soldering and tinning of metals, melting of thin-sheet carbon steel (Martins, Marelli, 2006; Kapustenko et al., 2011). Chlorine is released into the atmosphere much less frequently compared to the HCl (Taylor, 1988). Chlorides also end up in groundwater through irrigation (Karaivazoglou et al., 2005; Cayanan et al., 2008) and as a result of the use of salts for ice control on roads (Davison, 1971). One square meter of pavement receives from 50 to 70 g, but during the winter period, 0.6–2.7 kg of salt is used (Artamanov, 1986).

Under the conditions of atmospheric air pollution, plants can absorb chlorides with their leaves, and they accumulate more actively compared to sulfur, and the fluorides are more active compared to chlorides (Guderian, 1979).

The accumulation of chlorine in plants causes structural and physiological deviations (Hindawi, 1968; Endress et al., 1978a,b; Schreuder, Brewer, 2001a); decrease in growth rates (Schreuder, Brewer, 2001b); yields (Vijayan, Bedi, 1989). However, despite the negative impact of industrial emissions on plants (Yusypiva, Miasoid, 2019; Fedorchak, 2020), the successful invigoration of the environment is possible by combining technical and biological methods of plant protection. The work of many researchers had shown that green plantations are essential for cleansing the environment from harmful effects of toxic gases, dust and so on (Il'kun, 1978; Nikolaevskiy, 1979; Sergeychyk, 1984; Bessonova, Zaytseva, 2008; Levon, 2014; Sklyarenko, Bessonova, 2018).

Determination of the level of chlorine accumulation in the leaves of plants is important not only for assessing the potential purifying role of woody plant species under the technogenic conditions, but also for the purpose of detecting the bioindicators of contamination by its compounds.

The aim of this study is to analyze the level of chlorine accumulation in the leaves of woody plants growing in the area of green plantations of sanitary protection zones of industrial enterprises and identify the more descriptive bioindicators of atmospheric air pollution.

Material and methods

The research was carried out in the sanitary protection zones of a number of enterprises in the city of Zaporizhzhya: Zaporizhzhya Titanium and Magnesium Combine (ZTMC), Zaporizhzhya Aluminium Combine (ZALK) PJSC, Zaporizhzhya Metallurgical Combine "Zaporizhstal" (Zaporizhstal) PJSC, Zaporizhzhya Ferroalloy Plant (ZFER) PJSC, which belong to the first toxicity class; Zaporizhzhya Abrasive Combine (ZABR) PJSC belongs to the second class, Private joint-stock company "Vohnetryv-Soyuz" (Vohnetryv) – the third; "Ukrainian Graphite" (Ukrgrafit) PJSC, Zaporizhtransformator (ZATR) PJSC – the fourth. Subsequently, the abbreviated names of these companies will be predominantly used.

Such enterprises as "Zaporizhzhya Aluminium Combine" PJSC, Zaporizhzhya Metallurgical Combine "Zaporizhstal" PJSC, Zaporizhzhya Ferroalloy Plant PJSC, "Ukrainian Graphite" PJSC, Vohnetryv and Zaporizhzhya Titanium and Magnesium Combine are located in the industrial region, thereby forming an industrial complex. ZTMC, ZABR and ZATR are located within a certain distance from this group of enterprises – 3, 6 and 8 km respectively. We selected the forest band that was located 12 km away from any sources of pollution as our control area.

The objects of the study were selected on the basis of certain woody plants growing in all or most of the sanitary protection zones under consideration and the fact that their ratios in any given plantation were also quite large: *Acer* *negundo* L., *A. platanoides* L., *Aesculus hippocastanum* L., *Ailanthus altissima* Mill., *Armeniaca vulgaris* Lam., *Betula pendula* Roth., *Catalpa bignonioides* Walter, *Elaeagnus angustifolia* L., *Fraxinus lanceolata* Borkh., *Juglans regia* L., *Malus sylvestris* (L.) Mill., *Morus alba* L., *Platanus orientalis* Wiild., *Populus alba* L., *P. nigra* L., *P. simonii* Carr., *Robinia pseudoacacia* L., *Salix alba* L., *Tilia cordata* Mill., *Ulmus carpinifolia* Rupp., *U. laevis* Pall. At each site, five model trees of the same age category of each species were selected. The leaves needed in order to determine the chlorine content were taken from the south-eastern side of the crown at a height of 2 meters above the soil surface under the same lighting conditions. The first 3 leaves from the base of one-year shoots were used. The chlorine content in leaves was determined using the argentometric method (Pochynok, 1976).

The obtained data was processed according to the generally accepted methods of statistical variance using ANOVA and Tukey's honestly significant difference test criterion.

Results and discussion

The difference in the accumulation of chlorine in the leaves of the investigated species in the control group appears to be minor. In general, its content varies from 0.15 to 0.25% of the absolute dry mass. The smallest number is found in *Catalpa bignonioides* and *Betula pendula*, while the biggest – at *Ailanthus altissima* (Table 1). It should be noted that chlorine is an essential element of a plant's vital activity (Chen et al., 2008). The physiological role of chlorides in the plant organism is associated with the participation in a variety of metabolic reactions. One of such functions is being involved in the process of photosynthesis. Chlorine is necessary for the operation of the type II pigment system at the stage of water decomposition and the release of oxygen (Ort, Govindji, 1987). Chlorides particularly affect the work of H+/ATP phase of the tonoplast. It is thought that one of the mechanisms of chlorine influence on plant growth is related to the regulation of proton pump (Bityutskiy, 2014), the emergence of an action potential (Oprytov et al., 1991; White, Broadley, 2001). Chloride is a major osmotically active element in the vacuole and is involved in turgor, osmotic regulation and the proper functioning of stomata (Chen et al., 2008; Franco-Navarro, 2016; Eisenach, Angeli, 2017). However, as far as concentrations exceeding optimal levels are concerned, the element is observed to possess a certain degree of phytotoxicity.

We studied the dynamics of accumulation of chlorine in the leaves of such plant species as *Robinia pseudoacacia*, *Ulmus carpinifolia*, *Betula pendula,* and *Tilia cordata*, which grow under the conditions of the sanitary protection zone of Zaporizhzhya Titanium-Magnesium Combine that, compared to other enterprises, is responsible for the pollution of atmosphere with chlorides to the greatest extent. (Eydenzon, 1964; Habashi, 2016; Sahu et al., 2006.). These species were chosen specifically on account of them being a part of tree stands of almost all of our experimental sites. According to the data obtained, all of the woody plant species that grow in the area of sanitary protection zones with different levels of chlorine content are observed to have a tendency of reduction in the rate of accumulation of chlorine in their leaves during the vegetation period (Fig. 1). We have established a gradual accumulation of the element during the vegetation period, which happens to be the most intense in mature leaves, which have already finished growing (Fig. 1). In senescent leaves, the intensity of accumulation of the element decreases. Consequently, the largest amount of chlorine is detected at the end of the vegetation period, which is consistent with the results of Il'kun (1978) that he has obtained for a total of five woody plant species, two of which are included in our list as well – *Populus nigra* and *Salix alba*. This indicates that in order to ascertain the a)

b)

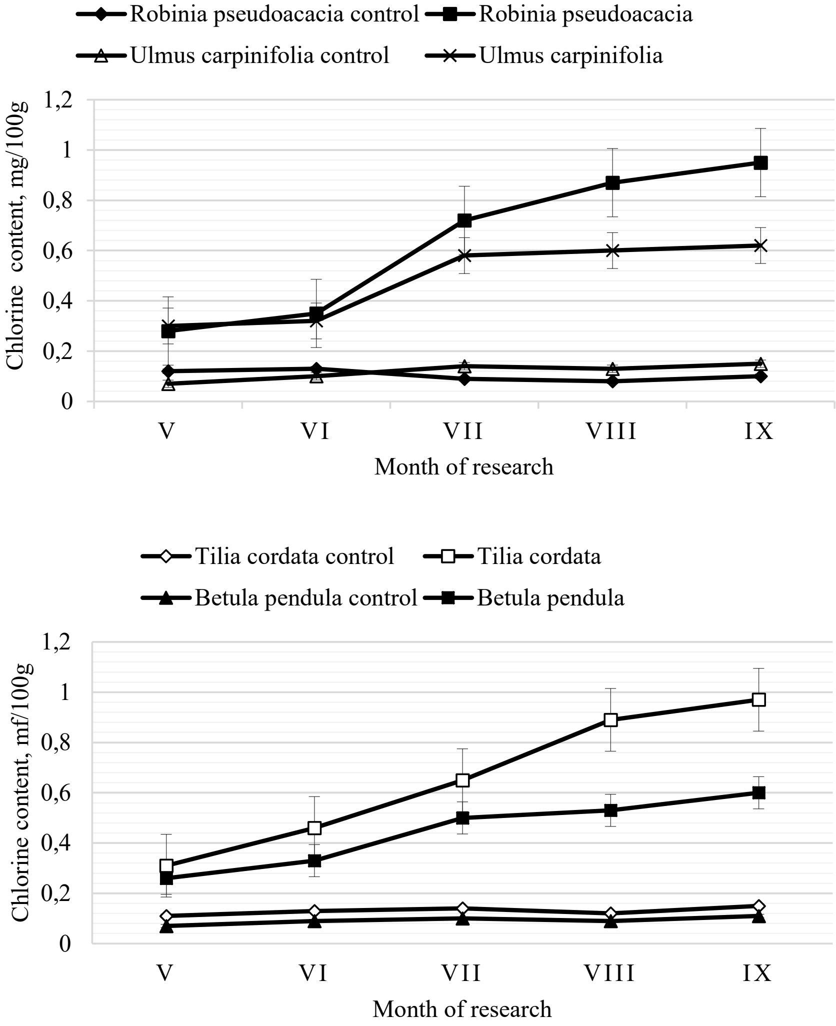

Fig. 1. Dynamics of chlorine content in the leaves of woody plants in the area of ZTMC sanitary protection zone (M ± m, n = 4).

role of woody plants in purifying the environment, it is best to carry out the analysis of the content of this element in their leaves during this period.

As can be seen from the Table 1, the chlorine content of the plant leaves in all of the investigated plantations of sanitary protection zones of industrial enterprises exceeds the levels found in control samples (the difference is statistically significant at the significance level of

0.05), except for the data for *Morus alba* and *Populus nigra*, which grow near the Zaporozh-transformator (ZATR) plant. It is known that plants are capable of absorbing chlorides with their leaves under the conditions of atmospheric air pollution through their stomata. But a small amount of gaseous harmful substances can penetrate the epidermis under certain conditions (Influence of pollution on vegetation, 1981).

Evidently, the differences in chlorine content in the leaves of a significant number of trees of protective forest bands of such enterprises as ZABR, ZALK, Ukrgrafit are not statistically reliable. There has also been no difference between the levels of chlorine in plants that grow in the area of sanitary protection zones of Zaporizhzhya Ferroalloy Plant (ZFER) and Zaporizhstal. Perhaps this is due to the fact that these industrial objects are situated close to each other.

Therefore, the greatest amount of chlorine is found in the leaves of plant species of the ZTMC sanitary protection zone, since this plant relies heavily on its use in the production cycle (Eydenzon, 1964; Habashi, 2016; Bordbar et al., 2017), and sometimes unscheduled emissions also take place. A direct relationship between the dose of gas (Cl_2) and its content in the tissues of leaves has been established. As a matter of fact, Parpan and Yukhymchuk (1984) showed that the amount of chlorine in a given leaf blade is inversely proportional to the distance of a plant away from the source of pollution. Kapelyush and Bessonova (2007) also found that out of all the plants living near the places where the enterprises produce chlorides as a result of their operation, the leaves of *Platanus orientalis* accumulate the biggest amount of chlorine.

In terms of accumulation of toxins in the organs of assimilation by the species of woody plants under investigation, and thus, the degree of air pollution by the aforementioned pollutant, companies are ranked as follows: ZTMC > Vohnetryv > Zaporizhstal ≥ ZFER > ZALK ≥ ZABR ≥ Ukrgrafit > ZATR.

Comparison of the accumulation of chlorine in the leaves of various species of woody plants of sanitary protection zones of industrial enterprises indicates the specific nature of the absorption of phytotoxicants. Moreover, with the increase in the number of green plantations near various enterprises, for the most part, the pattern of species arrangement depending on the level of accumulation of chlorine is being preserved. Although for some of them, there is a deviation from the established hierarchy of the protective forest bands of certain enterprises.

As can be seen from the data obtained (Table 1), the maximum amount of chlorine, in comparison with other plant species, is accumulated by the leaves of the following species: *Acer negundo*, *A. platanoides*, *Ailanthus altissima*, *Armeniaca vulgaris*, *Fraxinus lanceolata*, *Robinia pseudoacacia, Tilia cordata*, and the least amount – *Salix alba*, *Populus nigra, Malus sylvestris, Elaeagnus angustifolia, Platanus orientalis.* The following species occupy the intermediate position between the two groups: *Aesculus hippocastanum, Betula pendula, Catalpa bignonioides, Juglans regia, Morus alba, Populus alba, P. simonii, Ulmus carpinifolia, U. laevis.*

From the point of view of phytoindication of atmospheric air pollution, there is an interest in such an indicator as the relative accumulation coefficient – the ratio of the content of the element in the leaves of plants in the area of pollution measured prior to the content

T a b l e 1. The content of chlorine in the leaves of woody plants growing in the area of sanitary protection zones of industrial enterprises, g/100 g (M ± m, n = 4).

Species of plants	Control	Industrial enterprises							
		ZTMC	Ukrgrafit	ZABR	ZALK	„ZFER“	Zaporizhstal	Vohnetryv	ZATR
Acer negundo	0.20±0.008^{a}	1.17±0.025^{b}	0.51±0.016^{c}	0.59±0.016^{d}	–	0.58±0.019^{cd}	0.60±0.020^{de}	0.90±0.024^{f}	–
Acer platanoides	0.23±0.007^{a}	0.98±0.024^{b}	0.45±0.014^{c}	0.46±0.013^{cd}	–	0.54±0.017^{e}	0.58±0.018^{ef}	0.80±0.019^{g}	0.41±0.013^{cd}
Aesculus hippocastanum	0.18±0.006^{a}	0.59±0.014^{b}	0.33±0.011^{c}	0.36±0.012^{cd}	0.39±0.015^{de}	0.40±0.013^{de}	0.38±0.011^{de}	0.48±0.014^{f}	0.29±0.009^{c}
Ailanthus altissima	0.25±0.008^{a}	1.05±0.021^{b}	0.42±0.014^{c}	–	0.52±0.017^{e}	0.52±0.015^{e}	0.58±0.017^{ef}	0.87±0.021^{g}	0.40±0.014^{c}
Armeniaca vulgaris	0.17±0.007^{a}	0.72±0.016^{b}	–	0.40±0.015^{cd}	–	–	0.60±0.018^{e}	–	0.29±0.012
Betula pendula	0.15±0.006^{a}	0.60±0.014^{b}	0.33±0.010^{c}	0.35±0.012^{cd}	0.31±0.011^{cd}	0.37±0.015^{de}	0.39±0.012^{df}	0.50±0.016^{g}	0.27±0.011^{e}
Catalpa bignonioides	0.16±0.010^{a}	0.80±0.017^{b}	0.36±0.13^{c}	0.33±0.014^{cd}	–	0.48±0.17^{e}	0.42±0.013^{ef}	0.56±0.014^{g}	0.28±0.013^{d}
Elaeagnus angustifolia	0.21±0.011^{a}	0.48±0.012^{b}	0.30±0.012^{c}	0.28±0.011^{cd}	0.42±0.014^{e}		0.39±0.012^{ef}	0.46±0.012^{be}	0.29±0.011^{cd}
Fraxinus lanceolata	0.24±0.007^{a}	0.99±0.022^{b}	–	–	0.56±0.016^{cd}	0.52±0.018^{de}	0.52±0.016^{de}	0.71±0.017^{f}	0.33±0.012
Juglans regia	0.17±0.009^{a}	0.72±0.019^{b}	0.39±0.015^{c}	0.34±0.014^{cd}	–	–	0.61±0.017^{e}	0.51±0.013^{f}	0.34±0.010^{cd}
Malus sylvestris	0,23±0.010^{a}	0.58±0.015^{b}	0.30±0.013^{c}	0.29±0.012^{cd}	–	–	–	–	–
Morus alba	0.23±0.009^{a}	0.73±0.018^{b}	0.40±0.014^{c}	0.35±0.015^{cd}	0.31±0.015^{de}	0.36±0.013^{cd}	0.40±0.013^{cd}	0.61±0.019^{f}	0.26±0.008^{ae}
Platanus orientalis	0.20±0.007^{a}	–	–	–	–	–	–	0.42±0.014^{b}	–
Populus alba	0.17±0.008^{a}	0.70±0.015^{b}	0.38±0.011^{c}	–	0.40±0.012^{cd}	0.33±0.017^{ce}	0.38±0.014^{cd}	0.52±0.016^{f}	0.32±0.011^{e}
Populus nigra	0.17±0.011^{a}	0.49±0.014^{b}	0.31±0.013^{c}	–	0.33±0.010^{cd}	0.30±0.015^{cd}	0.33±0.011^{cd}	0.39±0.014^{e}	0.25±0.009^{ae}
Populus simonii	0.21±0.006^{a}	0.68±0.012^{b}	0.36±0.015^{c}	–	0.39±0.011^{cd}	0.30±0.011^{e}	0.32±0.013^{ce}	0.48±0.012^{f}	0.28±0.010^{e}
Robinia pseudoacacia	0.21±0.08^{a}	0.95±0.021^{b}	0.38±0.012^{c}	0.39±0.016^{d}	0.48±0.013^{e}	0.50±0.014^{ef}	0.56±0.015^{fg}	0.71±0.019^{h}	0.36±0.011^{cd}
Salix alba	0.22±0.007^{a}	0.45±0.012^{b}	0.32±0.011^{c}	0.30±0.013^{cd}	0.46±0.015^{be}		0.30±0.012^{cd}	0.40±0.015^{be}	0.36±0.014^{cd}
Tilia cordata	0.25±0.008^{a}	0.97±0.020^{b}	0.44±0.014^{c}	0.48±0.015^{cd}	0.45±0.011^{cd}	0.59±0.015^{e}	0.53±0.015^{de}	0.76±0.021^{f}	0.40±0.013^{ce}
Ulmus carpinifolia	0.24±0.007^{a}	0.62±0.016^{b}	0.32±0.015^{c}	0.42±0.012^{d}	0.43±0.012^{de}	0.40±0.011^{de}	0.42±0.014^{de}	0.51±0.016^{f}	0.34±0.012^{c}
Ulmus laevis	0.22±0.009^{a}	0.63±0.014^{b}	0.36±0.011^{c}	–	0.44±0.014^{d}	–	0.41±0.012^{de}	–	–

Notes: – this species of trees is absent; different letters indicate values reliably differing from each other within a single line of the table based on the results of using the Tukey’s test ($P < 0.05$).

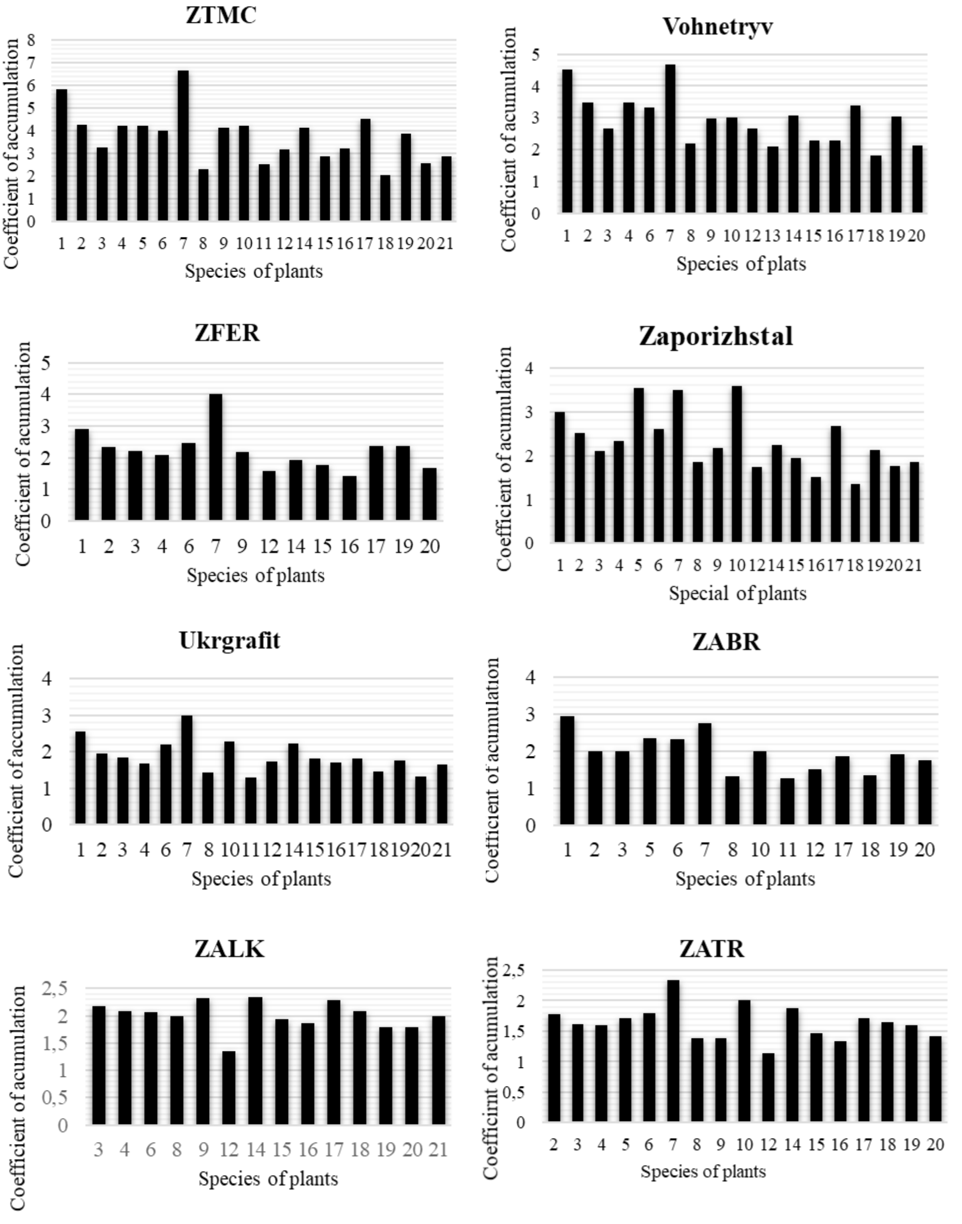

Fig. 2. Magnitude of the relative accumulation of toxicant (1 – *Acer negundo*; 2 – *Acer platanoides*; 3 – *Aesculus hippocastanum;* 4 – *Ailanthus altissima*; 5 – *Armeniaca vulgaris*; 6 – *Betula pendula*; 7 – *Catalpa bignonioides*; 8 – *Elaeagnus angustifolia*; 9 – *Fraxinus* lanceolata; 10 – *Juglans regia*; 11 – *Malus sylvestris;* 12 – *Morus alba*; 13 – *Platanus orientalis*; 14 – *Populus alba*; 15 – *Populus nigra*; 16 – *Populus simonii*; 17 – *Robinia pseudoacacia*; 18 – *Salix alba*; 19 – *Tilia cordata;* 20 – *Ulmus carpinifolia*; 21 – *Ulmus laevis*).

measured in the control sample. Its highest values are found in such species of plants as *Catalpa bignonioides, Acer negundo* and *Robinia pseudoacacia*, *Juglans regia, Populus alba*. These plants can be specifically used as informative phytoindicators of air pollution by chlorides. The smallest coefficient of relative accumulation of an element is found in *Salix alba*, *Malus sylvestris* and *Elaeagnus angustifolia, Morus alba.*

Higher absolute content of an element in the organs of plants characterizes their superior role as a purifying agent. The following plant species can be considered to satisfy the aforementioned criterion: *Acer negundo, Ailanthus altisima, Fraxinus lanceolata, Tilia cordata.* The chlorine content in the leaves of plants growing in the area near the ZTMC exceeds 0.90%, where the assortment of plants is represented most fully as a consequence of the level of accumulation of chlorine being the highest there.

Conclusion

Accumulation of chlorine in the leaves of woody plant species growing in the area of sanitary protection zones of the Zaporizhzhya industrial region occurs during the entire vegetation period, being the most active in mature leaves that have finished growing. The maximum amount of element is detected at the end of the vegetation season.

The leaves of plants of the plantations of sanitary protection zones of different enterprises under investigation accumulate more chlorine compared to the plants of the control group. In terms of chlorine content in the leaves of plants under investigation, and thus, the degree of air pollution by the aforementioned pollutant, sanitary protection zones of enterprises are ranked as follows: ZTMC > Vohnetryv > Zaporizhstal ≥ ZFER > ZALK ≥ ZABR ≥ Ukrgrafit > ZATR.

Species of woody plants were divided into three groups according to the chlorine content in their leaves: I – the maximum level – *Acer negundo*, *A. platanoides*, *Ailanthus altissima*, *Armeniaca vulgaris*, *Fraxinus lanceolata*, *Robinia pseudoacacia, Tilia cordata*, II – the medium level – *Aesculus hippocastanum, Betula pendula, Catalpa bignonioides*, *Juglans regia*, *Morus alba*, *Populus alba*, *P. simonii*, *Ulmus carpinifolia*, *U. laevis*, III – the minimum level – *Salix alba*, *Populus nigra, Malus sylvestris, Elaeagnus angustifolia, Platanus orientalis.* Groups of plants with the highest rates of accumulation of chlorides can be recommended for the purpose of purification of atmospheric air from these pollutants.

The highest coefficient of relative chlorine accumulation is found in such species of plants as *Catalpa bignonioides, Acer negundo* and *Robinia pseudoacacia*, *Juglans regia, Populus alba*. These plants have a potential to be used specifically as phytoindicators of pollution by chlorides. The smallest such coefficient is found in *Salix alba*, *Malus sylvestris* and *Elaeagnus angustifolia, Morus alba.*

The obtained results can be used for the development of recommendations with the purpose of selecting the assortment of woody plants for the reconstruction of green plantations growing in the area of sanitary protection zones of enterprises

In the future, the accumulation of such pollutants of atmospheric air as fluorine and phenol in the leaves of woody plant species growing in the area of protective forest belts will be investigated.

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