

## Accumulation of sulfur and glutathione in leaves of woody plants growing under the conditions of outdoor air pollution by sulfur dioxide

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In the course of human industrial activity, atmospheric air is polluted by gaseous pollutants, among which sulfur compounds, and sulfur dioxide (SO<sub>2</sub>) in particular, play a key role. Vegetation is a universal filter that is capable, in conjunction with certain technical facilities, of protecting the environment from pollution by the ingredients of industrial emissions. The purpose of this work is to determine the level of accumulation of sulfur and glutathione in the leaves of woody plants growing in the areas of sanitary protection zones of enterprises of the city of Zaporizhzhya in order to develop recommendations for the creation of an effective biofilter. The objects of the study were the woody plant species growing in the area of protective plantations of a number of enterprises in Zaporizhzhya: RE Zaporizhzhya Titanium & Magnesium Combine, Zaporizhzhya Aluminium Plant PJSC, Zaporizhzhya Abrasive Plant PJSC, Zaporizhstal PJSC, Zaporizhzhya Ferroalloy Plant PJSC, Zaporizhvohnetryv PJSC, PrJSC "Ukrgrafit" and Zaporizhtransformator PJSC. The control area was a forest belt located 12 km away from the source of pollution. At each site 5 model trees of a given age category of each species were selected. The leaves needed in order to determine the sulfur content were taken from the south-eastern side of the crown at a distance of 2 m above the soil surface under the same lighting conditions. We have established that the accumulation of sulfur in leaves of woody plants which grow under the conditions of outdoor air pollution by sulfur dioxide (SO<sub>2</sub>) occurs during the entire vegetation period, with the young leaves that have just finished growing being the most affected. The maximum amount of sulfur is observed at the end of the growing season. The greater concentration of sulfur in the leaves of woody plants in the areas of sanitary protection zones of industrial enterprises is linked to the higher level of gaseous pollutant emissions in the atmosphere of a given enterprise, but the degree of increase in the content of the pollutant in the leaves of plants of various protective plantations is not proportional to the quantitative indicators of the level of sulfur dioxide (SO<sub>2</sub>) in the air. Woody plant species were divided into three groups according to the amount of sulfur accumulated in their leaves: I – the maximum level – *Betula pendula*, *Tilia cordata*, *Salix alba*, *Robinia pseudoacacia*, *Populus alba*, *P. simonii*, *P. nigra*, II – medium – *Acer platanoides*, *A. negundo*, *Fraxinus lanceolata*, *Catalpa bignonioides*, III – the smallest – *Morus alba*, *Ailanthus altissima*, *Elaeagnus angustifolia* and *Ulmus carpinifolia*. The increase in sulfur content in the leaves of woody plants growing in the area of sanitary protection zones is consistent with the increase in glutathione content compared to our control parameters, which is not only of high physiological significance, but its formation can also be one of the ways of metabolizing this element. 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 a subsequent study, the accumulation of gaseous pollutants such as chlorine and phenol in the leaves of woody plants growing in and around protective forest belts will be examined.

**Keywords:** sanitary protection zones; green plantations; accumulation; sulfur compounds

### Introduction

In the course of human industrial activity, atmospheric air is polluted by gaseous pollutants, among which sulfur compounds, and sulfur dioxide (SO<sub>2</sub>) in particular, play a key role. Sulfur dioxide is released into the atmosphere during combustion of coal and lignite, oil and petroleum products, and also timber, as a result of the production of sulfuric acid and the smelting of sulfur-containing ores (Liu et al., 2018). A significant amount of this compound is released into the environment during the operation of thermal power plants, enterprises of ferrous and nonferrous metallurgy, cement, coke, chemical plants etc. (Il'kun, 1978; Subba et al., 2016; Martynov & Brygadyrenko, 2017; Tuygun et al., 2017). For example, smelting 1 ton of pig iron is accompanied by an average of 22.4 kg of sulfur dioxide (Kaljuzhnyj, 1981).

Vegetation is a kind of universal filter that is capable, in conjunction with certain technical facilities, of protecting the environment from pollution by the ingredients of industrial emissions (Kozjukina et al., 1980; Bessonova & Zajceva, 2008; Mitchell et al., 2010). It acts as a kind of buffer that smooths the fluctuations of the pollutant's concentration in the air (Simon et al., 2011; Hwangbojun et al., 2016; Stratu et al., 2016;

Faly et al., 2017). The buffer capacity of plants is proportional to the absorption capacity of the pollutants (Tarabrin et al., 1986). Among the sulfur compounds, the one that is most easily absorbed by the leaves is SO<sub>2</sub>, followed by H<sub>2</sub>S, with CS<sub>2</sub> being the least active. The last two pollutants are much less common (Sergejchik et al., 1998; Li et al., 2016). The driving force behind their absorption capacity is the diffusion of molecules, where they are assimilated by cells thereby entering the metabolism (Okpodu et al., 1999; Baciak et al., 2015).

Each species of plant has its own inherent cut-off point for the accumulation of any given pollutant. This indicator should be taken into account when creating plantations in the areas that are part of sanitary protection zones of industrial enterprises. Taking into account the gas-absorbing capacity of certain types of woody plants is an important condition for the creation of effective biofilters in order to achieve the maximum sanitary and hygienic effect (Kulagin, 1970; Paul, 1974). The intensity of gas absorption depends not only on the physiological and biochemical characteristics of plants, but also on the concentration of pollutants (Hwangbo et al., 2000; Cicek & Koparal, 2004), the duration of their action and environmental conditions during their growth (Il'kun, 1978; Smit, 1985; Getko, 1989). This makes it difficult to develop uniform

recommendations even for similar enterprises in different climatic zones. In each particular case, plant groups will perform their function with a varying degree of effectiveness. Therefore, the recommendations for the planting of greenery should have an exact environmental context, although certain general patterns do exist. Some researchers believe that the content of sulfates in plants should be used to evaluate functional changes that are not being detected via visual observation (Tripodo et al., 1992) or as an indicator of the pollutant's activity (Pöykiö & Torvela, 2001).

The aim of this work is to determine the level of accumulation of sulfur and glutathione in the leaves of woody plants growing in the areas of sanitary protection zones of enterprises of the city of Zaporizhzhya in order to develop recommendations for the creation of an effective biofilter.

## Materials and methods

The research was carried out in the sanitary protection zones of a number of enterprises in the city of Zaporizhzhya: RE Zaporizhzhya Titanium & Magnesium Combine (ZTMC), Zaporizhzhya Aluminium Plant (ZALK) PJSC, Zaporizhstal PJSC, Zaporizhzhya Ferroalloy Plant (ZFER) PJSC, which belong to the 1st enterprise hazard class, Zaporizhzhya Abrasive Plant (ZABR) PJSC – 2nd, Zaporizhovnetriv-SOYUZ PJSC (Vohnetryv) – the 3rd, PrJSC "Ukrgrafit" and Zaporizh-transformator (ZATR) PJSC – 4th.

From this point, the abbreviated names of these companies will be mostly used. The level of SO<sub>2</sub> emissions by these enterprises varies significantly. Zaporizhstal and Zaporizhzhya Ferroalloy Plant emit the largest amounts of dioxide and other sulfur compounds – 4993.004 and 1178.706 tons per year, respectively. Other plants can be arranged in order of decreasing number of these pollutants in the following way: Ukrgrafit (162.984), ZABR (159.988), Vohnetryv (149.220), ZTMC (101.635), ZALK (67.223), ZATR (0.065).

Such enterprises as Zaporizhzhya Aluminium Plant PJSC, Zaporizhstal PJSC, Zaporozhye Ferroalloy Plant PJSC, PrJSC "Ukrgrafit", "Vohnetryv" and Zaporizhzhya Titanium and Magnesium Combine are located in the factory district, forming an industrial complex, and therefore the degree of air pollution by gaseous sulfur compounds in the sanitary protection zones differs less compared to the volumes of this particular phytotoxicant being emitted by each plant individually. This group of enterprises is separated at the following distances: ZTMC (3 km), ZABR (6 km) and ZATR (8 km). The control area was a forest belt located 12 km away from the source of pollution.

Woody plants that grow in the areas of the sanitary-protective zones of all or most enterprises and had a large enough share in the plantations were chosen as the objects of study: *Ailanthus altissima* Mill., *Betula pendula* Roth., *Ulmus carpinifolia* Rupp., *Catalpa bignonioides* Walter, *Acer platanoides* L., *Acer negundo* L., *Tilia cordata* Mill., *Elaeagnus angustifolia* L., *Robinia pseudoacacia* L., *Populus alba* L., *Morus alba* L., *Fraxinus lanceolata* Borkh., *Salix alba* L., *Populus simonii* Carr. and *Populus nigra* L. At each site, 5 model trees of a given age category of each species were selected. The leaves needed in order to determine the sulfur content were taken from the south-eastern side of the crown at a distance of 2 m above the soil surface under the same lighting conditions. The first three leaves from the base of one-year shoots were used. The content of sulfur was determined by the weight method (Mochalova, 1975), the reduced glutathione – by the titrimetric method. Statistical data analysis was carried out using the Gnumeric software package.

## Results

We have studied the dynamics of change in the content of sulfur during the vegetation period in the leaves of plants growing in the area of the sanitary protection zone of the "Zaporizhstal" plant, which emits into the atmosphere the largest amount of this pollutant, with the aim of calculating the sampling time in order to determine the role of certain woody plant species in purifying the atmospheric air from gaseous sulfur compounds. It was found that the content of sulfur in the assimilating organs of plants in the process of vegetation did increase, but at a different rate depending on the phase of their ontogenesis (Fig. 1). During the period of intense growth, the amount of sulfur was less than

in the young leaves that had already finished growing. The section of the curve, which reflects the process of accumulation of sulfur in young leaves, whose growth has already ceased, appears to be the most steep (Fig. 1). Similar dynamics of sulfur accumulation were characteristic of four species of plants, the leaves of which were used to study this process – *B. pendula*, *A. hippocastanum*, *R. pseudoacacia* та *M. alba*. The maximum content of sulfur in the leaves of all plants was detected at the end of the vegetation period (Fig. 1).

The results of our research show that despite the short distance of a number of plants from each other and the spread of sulfuric anhydride in the adjacent sanitary protection zones, the highest concentration of total sulfur is found in the leaves of plants of the protective forest belts of the "Zaporizhstal" plant and to a lesser degree – of ZFER, which emit the largest amount of this pollutant into the environment (Table 1).

**Table 1**

The content of sulfur in the leaves of woody plants growing in the area of sanitary protection zones of industrial enterprises (% out of absolute dry mass,  $\bar{x} \pm SE$ ,  $n = 4$ )

Species of plant	Industrial enterprises							
	Control	ZTMC	Ukr-grafit	ZABR	ZALK	ZFER	Zaporizhstal	Vohnetryv
<i>Acer negundo</i>	0.12 ± 0.30 ± 0.007 <sup>a</sup>	0.30 ± 0.011 <sup>b</sup>	0.38 ± 0.015 <sup>c</sup>	0.33 ± 0.008 <sup>bc</sup>	–	–	0.56 ± 0.009 <sup>d</sup>	0.30 ± 0.014 <sup>e</sup>
<i>Acer platanoides</i>	0.14 ± 0.005 <sup>a</sup>	0.35 ± 0.008 <sup>b</sup>	0.40 ± 0.009 <sup>c</sup>	0.34 ± 0.013 <sup>bd</sup>	–	0.63 ± 0.011 <sup>c</sup>	0.69 ± 0.012 <sup>f</sup>	0.36 ± 0.007 <sup>g</sup>
<i>Aesculus hippocastanum</i>	0.13 ± 0.006 <sup>a</sup>	0.32 ± 0.007 <sup>b</sup>	–	0.44 ± 0.011 <sup>c</sup>	0.36 ± 0.006 <sup>d</sup>	0.51 ± 0.015 <sup>e</sup>	0.56 ± 0.010 <sup>f</sup>	0.34 ± 0.012 <sup>g</sup>
<i>Ailanthus altissima</i>	0.11 ± 0.005 <sup>a</sup>	0.25 ± 0.005 <sup>b</sup>	0.30 ± 0.007 <sup>c</sup>	–	0.27 ± 0.009 <sup>bd</sup>	0.39 ± 0.010 <sup>c</sup>	0.48 ± 0.013 <sup>f</sup>	0.26 ± 0.008 <sup>de</sup>
<i>Betula pendula</i>	0.11 ± 0.007 <sup>a</sup>	0.45 ± 0.010 <sup>b</sup>	–	–	0.50 ± 0.010 <sup>c</sup>	0.80 ± 0.012 <sup>d</sup>	0.97 ± 0.014 <sup>e</sup>	0.47 ± 0.010 <sup>f</sup>
<i>Catalpa bignonioides</i>	0.14 ± 0.009 <sup>a</sup>	–	–	0.48 ± 0.009 <sup>b</sup>	0.39 ± 0.014 <sup>c</sup>	0.55 ± 0.011 <sup>d</sup>	0.67 ± 0.008 <sup>e</sup>	0.30 ± 0.007 <sup>f</sup>
<i>Elaeagnus angustifolia</i>	0.09 ± 0.006 <sup>a</sup>	–	0.28 ± 0.006 <sup>b</sup>	0.25 ± 0.010 <sup>c</sup>	–	0.45 ± 0.012 <sup>d</sup>	0.47 ± 0.007 <sup>de</sup>	0.25 ± 0.009 <sup>ef</sup>
<i>Fraxinus lanceolata</i>	0.08 ± 0.005 <sup>a</sup>	0.30 ± 0.009 <sup>b</sup>	0.40 ± 0.010 <sup>c</sup>	–	0.34 ± 0.007 <sup>d</sup>	0.61 ± 0.010 <sup>e</sup>	0.62 ± 0.014 <sup>e</sup>	–
<i>Juglans regia</i>	0.16 ± 0.007 <sup>a</sup>	0.25 ± 0.005 <sup>b</sup>	–	0.30 ± 0.014 <sup>c</sup>	–	–	0.58 ± 0.011 <sup>d</sup>	0.30 ± 0.013 <sup>de</sup>
<i>Morus alba</i>	0.10 ± 0.009 <sup>a</sup>	0.21 ± 0.006 <sup>b</sup>	0.27 ± 0.006 <sup>c</sup>	0.23 ± 0.008 <sup>bd</sup>	0.19 ± 0.005 <sup>bc</sup>	0.33 ± 0.008 <sup>f</sup>	0.44 ± 0.007 <sup>g</sup>	0.23 ± 0.009 <sup>bd</sup>
<i>Populus alba</i>	0.15 ± 0.007 <sup>a</sup>	0.46 ± 0.015 <sup>b</sup>	0.61 ± 0.007 <sup>c</sup>	0.55 ± 0.010 <sup>d</sup>	0.45 ± 0.009 <sup>de</sup>	0.89 ± 0.015 <sup>f</sup>	0.96 ± 0.015 <sup>g</sup>	0.41 ± 0.010 <sup>be</sup>
<i>Populus nigra</i>	0.14 ± 0.009 <sup>a</sup>	0.40 ± 0.008 <sup>b</sup>	0.49 ± 0.011 <sup>c</sup>	0.47 ± 0.010 <sup>cd</sup>	0.37 ± 0.015 <sup>de</sup>	–	1.05 ± 0.014 <sup>f</sup>	0.42 ± 0.013 <sup>g</sup>
<i>Populus simonii</i>	0.16 ± 0.005 <sup>a</sup>	0.37 ± 0.009 <sup>b</sup>	0.45 ± 0.009 <sup>c</sup>	0.40 ± 0.15 <sup>bd</sup>	0.37 ± 0.011 <sup>cd</sup>	0.86 ± 0.013 <sup>d</sup>	0.93 ± 0.012 <sup>f</sup>	0.35 ± 0.008 <sup>bd</sup>
<i>Robinia pseudoacacia</i>	0.12 ± 0.009 <sup>a</sup>	0.41 ± 0.011 <sup>b</sup>	0.51 ± 0.010 <sup>c</sup>	0.58 ± 0.013 <sup>d</sup>	0.42 ± 0.012 <sup>de</sup>	0.85 ± 0.014 <sup>f</sup>	0.90 ± 0.013 <sup>g</sup>	0.39 ± 0.010 <sup>h</sup>
<i>Salix alba</i>	0.14 ± 0.006 <sup>a</sup>	0.33 ± 0.006 <sup>b</sup>	0.42 ± 0.013 <sup>c</sup>	–	0.32 ± 0.007 <sup>bd</sup>	0.73 ± 0.013 <sup>d</sup>	0.81 ± 0.013 <sup>f</sup>	0.21 ± 0.006 <sup>g</sup>
<i>Tilia cordata</i>	0.15 ± 0.006 <sup>a</sup>	0.41 ± 0.007 <sup>b</sup>	0.50 ± 0.011 <sup>c</sup>	–	0.40 ± 0.013 <sup>bd</sup>	–	1.02 ± 0.010 <sup>f</sup>	0.38 ± 0.007 <sup>bd</sup>
<i>Ulmus carpinifolia</i>	0.13 ± 0.008 <sup>a</sup>	0.23 ± 0.010 <sup>b</sup>	0.29 ± 0.008 <sup>c</sup>	0.27 ± 0.007 <sup>cd</sup>	0.21 ± 0.005 <sup>bc</sup>	0.40 ± 0.007 <sup>f</sup>	0.47 ± 0.006 <sup>g</sup>	0.20 ± 0.006 <sup>bc</sup>

Note: "–" – this species of tree 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 test ( $P < 0.05$ ).

The lowest amount of sulfur was accumulated in the leaves of woody plants growing in the areas of sanitary protection zones of such enterprises as ZATR, ZTMC and ZALK. As can be seen from the obtained data (Table 1), the maximum amount of sulfur, compared to other species of plants, accumulated in leaves of the following species: *B. pendula*, *T. cordata*, *R. pseudoacacia*, *P. alba*, *P. simonii*, *P. nigra*; and the minimum – *M. alba*, *A. altissima*, *E. angustifolia* and *U. carpinifolia*. The following species hold the intermediate position between the two groups: *A. platanoides*, *A. negundo*, *F. lanceolata*, *C. bignonioides*.

Analysis of the content of the tripeptide glutathione, which includes the sulfur-containing amino acid cysteine, in the leaves of 6 species of woody plants that grow in the areas of protective plantations of enterprises, and which varies according to the level of air pollution by sulfur

dioxide (SO<sub>2</sub>) (Zaporizhstal, ZFER, ZTMC and Vohnetryv), showed an increase in its amount compared to our control with the exception of *T. cordata*. In the leaves of this type, the concentration of the tripeptide, on the contrary, decreased as a result of high content of SO<sub>2</sub> in the air (Zaporizhtal and Vohnetryv), and slightly increased as a result of lower levels of the pollutant (ZTMC).

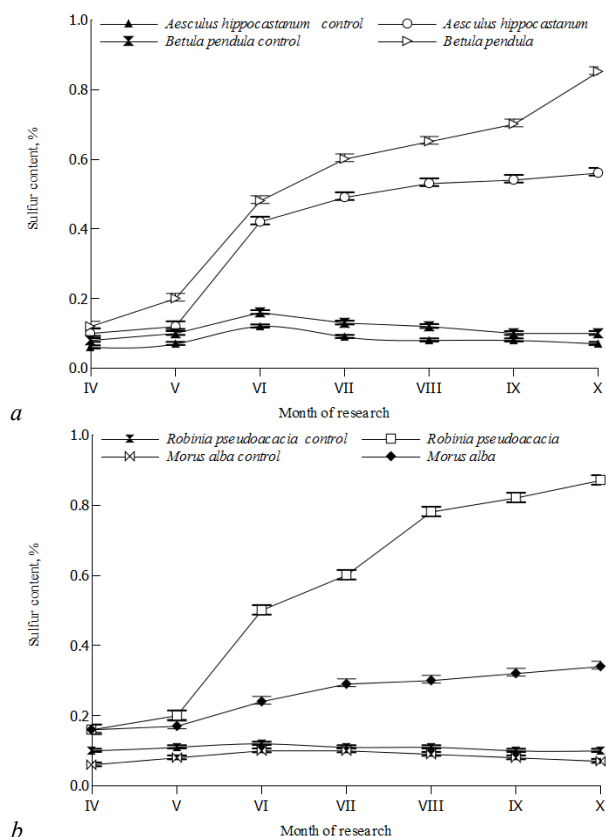


Fig. 1. Dynamics of sulfur content in leaves of woody plants during the vegetation period ( $x \pm SE$ ,  $n = 4$ )

Table 2

The content of glutathione (mg/%) in the leaves of plants growing in the area of sanitary protection zones of industrial enterprises ( $x \pm SE$ ,  $n = 4$ )

Species of plans	Control, x ± SE	Industrial enterprises					
		Zaporizhstal		Vohnetryv		ZTMC	
		x ± SE	Relativ e to control, %	x ± SE	Relative to control, %	x ± SE	Relative to control, %
<i>Ailanthus altissima</i>	89.12 ± 0.96 <sup>a</sup>	140.23 ± 1.12 <sup>b</sup>	157.3	128.42 ± 1.18 <sup>c</sup>	144.1	111.36 ± 0.96 <sup>d</sup>	125.0
<i>Fraxinus lanceolata</i>	33.60 ± 0.42 <sup>a</sup>	54.21 ± 0.68 <sup>b</sup>	161.3	44.12 ± 1.02 <sup>c</sup>	131.3	39.86 ± 0.62 <sup>d</sup>	118.6
<i>Morus alba</i>	40.36 ± 0.58 <sup>a</sup>	63.84 ± 0.71 <sup>b</sup>	158.2	53.45 ± 0.50 <sup>c</sup>	132.4	52.16 ± 0.66 <sup>c</sup>	129.2
<i>Robinia pseudoacacia</i>	67.18 ± 0.91 <sup>a</sup>	179.71 ± 1.12 <sup>b</sup>	267.5	153.69 ± 1.40 <sup>c</sup>	228.8	140.18 ± 0.89 <sup>d</sup>	208.7
<i>Tilia cordata</i>	45.89 ± 0.48 <sup>a</sup>	35.75 ± 0.63 <sup>b</sup>	77.9	39.56 ± 0.78 <sup>c</sup>	86.2	49.31 ± 0.57 <sup>d</sup>	107.5
<i>Ulmus carpinifolia</i>	53.73 ± 0.42 <sup>a</sup>	84.39 ± 0.72 <sup>b</sup>	157.1	70.36 ± 1.04 <sup>c</sup>	131.0	61.42 ± 0.65 <sup>d</sup>	114.3
<i>Populus nigra</i>	75.16 ± 0.52 <sup>a</sup>	195.91 ± 1.02 <sup>b</sup>	260.7	178.61 ± 1.31 <sup>c</sup>	237.6	149.99 ± 1.12 <sup>d</sup>	199.6

Note: see Table 1.

## Discussion

According to the data obtained, in the species of trees growing in the areas of sanitary protection zones with different levels of accumula-

tion of sulfur in their leaves there is a downward dynamic of its accumulation during the vegetation period (Fig. 1). During the period of intense leaf growth, this process occurred at a lower pace than in organs that had already completed growth. Perhaps this is due to the fact that during the growth of leaves the accumulation of mass is more intense than the accumulation of sulfur, that is, there may be involvement of the so-called "dilution" effect, which some researchers have observed in the case of the accumulation of lead (Hijano et al., 2005).

Subsequently (in July), the pace of accumulation of the element is reduced, eventually slowing down even further. It should be noted that, according to some researchers, young leaves during their growth and development most actively absorb sulfur dioxide (Malhotra & Hocking, 1976; Barahtenova, 1995), but according to others, the growth of sulfur content in leaves is most significant in the middle of the vegetation period (Vasfilov, 2013).

Thus, according to our data, the accumulation of the element in leaves occurs throughout the vegetation period, and its highest content is detected at the end of the vegetation period. This indicates that in order to calculate the role of plants as a universal biofilter, it is better to carry out the analysis of the content of this element in the leaves during the said period. The fact that the content of sulfur in the leaves of woody plants growing under the conditions of outdoor air pollution by sulfur compounds is at its maximum at the end of the vegetation period, is noted in other papers as well (Hijano et al., 2005; Kapeljush & Bessonova, 2007; Vasfilov, 2013).

It should be noted that the level of accumulation of sulfur in the leaves of plants does not accurately reflect their role as a biofilter. Some researchers point out that not all sulfur that is absorbed from the air is fixed in the leaves. A part of it is washed out by precipitation and released with moisture back into the atmosphere (Getko, 1989; Il'kun, 1978; Il'kun & Morgun, 1980). Sulfur accumulated in leaves in the form of SO<sub>2</sub> and H<sub>2</sub>S, can be used in metabolic processes, becoming a part of sulfur-containing amino acids and glutathione (Schiff & Hodson, 1973; Hock & Anderson, 1978; Kok et al., 1986) or moving to other organs in the form of sulfates (Brandle & Schnyde, 1970; Paul, 1976), as well as in the soil from the roots (Nikolaev, 1963; Cornis, 1968). However, most authors believe that the indicators of accumulation of sulfur in the leaves, on average, reflect the accumulative capacity of different species of plant, hence also their role as a biofilter (Al-Jahdali & Bin Bisher, 2008; Zhang et al., 2013; Likus-Cieřlik & Pietrzykowski, 2017). In our opinion, this is confirmed by the data obtained by Godzik (1976), obtained as a result of experiments with woody plants, which differ sharply from those of herbaceous plants. While studying the distribution of <sup>35</sup>S in birch, oak, coniferous plants (spruce, fir, yew), the author established that the transfer of sulfur to the trunk of trees did not occur, and the radioisotope of this element injected into the trunk was able to move within the leaf blade. On this basis, it is assumed that sulfur, which is absorbed by leaves of woody plants, appears to be less mobile compared to the way it behaves inside herbaceous plants, and its content in these organs more accurately reflects the level of accumulation of the element and the degree of air pollution of a given site using different methods of calculation, hence their role as a biofilter.

We have found that the higher level of pollutant in the air causes it to accumulate more in the leaves of plants (Table 1). This is consistent with the data of Vasfilov (2013), which establishes the fact that the level of accumulation of sulfur in the leaves during the entire vegetation period is proportional to the unit of crude and dry mass, the leaf area and the unit of mass of chlorophyll. Some other researchers also point to an increase in sulfur content in plant leaves with an increase in the concentration of SO<sub>2</sub> (Roberts, 1974; Paul, 1976; Bytnerowicz et al., 1987).

However, as can be seen from our data, the degree of increase in the content of the pollutant in the leaves of plants of various protective plantations was not proportional to the quantitative indicators of the level of SO<sub>2</sub> in the air. Perhaps this is due to the fact that its accumulation in plant leaves due to the absorption of SO<sub>2</sub> from the air within certain concentrations largely depends more on the time of the action of the pollutant on plants than on the increase of its concentration. Thus, Guderian (1979), notes that the accumulation of sulfur occurs at a higher rate given a longer exposure to it rather than due to the high gas



concentrations. This was also confirmed experimentally (Roberts, 1974), where it was established that leaves of *Fraxinus americana* and *Rhododendron obtusum japonicum* absorbed SO<sub>2</sub> from the outdoor air containing various concentrations of the pollutant (0.2, 0.5 and 1.0 mg/l) with roughly the same intensity.

Woody plant species were divided into three groups according to the amount of sulfur accumulated in their leaves: I – the maximum level – *B. pendula*, *T. cordata*, *S. alba*, *R. pseudoacacia*, *P. alba*, *P. simonii*, *P. nigra*, II – medium – *A. platanoides*, *A. negundo*, *F. lanceolata*, *C. bignonioides*, III – the smallest – *M. alba*, *A. altissima*, *E. angustifolia* and *U. carpinifolia*.

However, while comparing the level of accumulation of sulfur in the leaves of different species of woody plants, according to the literature data containing our results, as well as making a comparison of the parameters obtained by different authors, a certain number of problems arise. The lists of species of woody plants, the leaves of which were used to study the accumulation of sulfur by a number of researchers, differ and only some species in them are common, but they are not always properly placed within the groups with similar levels of accumulation of toxicants. For example, according to Korshikov (1995) the leaves of white mulberry growing under the technogenic conditions accumulate very little sulfur, but according to Tarabrin (1986) – the case is just the opposite. Kulagin (1970) places ash-leaved maple within the group of plants which poorly accumulate the said toxicant, whereas Getco (1989) claims it to be the plant that accumulates sulfur the most. According to other authors (Basovic et al., 1975), this species occupies an average position in the distribution of woody plants when the accumulation of sulfur in their leaves is taken as a criteria. Korshikov (1995) points out that the leaves of *A. pseudoplatanus* growing under environmental pollution accumulate little sulfur in relation to control, but according to Getco (1989) – they accumulate a considerable amount. Both Tarabrin (1986) and Getco (1989) note the high sulfur-accumulating ability of the assimilating organs of *R. pseudoacacia*, whereas Sergejchik (1997) considers it to be average. In some studies, the first group (maximum accumulation of sulfur) includes *T. cordata* (Tarabrin et al., 1986; Getco, 1989; Sergejchik, 1997) and *P. canadensis* (Tarabrin et al., 1986; Korshikov et al., 1995; Sergejchik, 1997), which is consistent with the data obtained by us. The discrepancy in the data obtained by different authors can be explained by the fact that experiments were carried out in different climatic zones and enterprises with a specific ratio of air pollutants, which affects the intensity of their accumulation.

If sulfur enters the leaf blade in the form of SO<sub>2</sub> or H<sub>2</sub>S, it is first oxidized to a sulfate (Hock & Anderson, 1978; Heber & Hüve, 1997). The process of assimilation of sulfate is preceded by its activation by phosphorylation. This reaction can be considered a "unique gate" through which the relatively inert sulfur oxide enters the metabolic cycle (Shiff & Hodson, 1973), while the concentration of glutathione and amino acids in plants increases. On the basis of experiments with the fumigation of plants H<sub>2</sub>S Kok (1986) believes that glutathione plays the role of spare sulfur, which can quickly be involved in metabolism. As can be seen from Table 2, the level of increase in the content of glutathione in the leaves of investigated plants is consistent with the magnitude of the accumulated sulfur. Thus, the content of sulfur in leaves of such species such as *R. pseudoacacia* and *P. nigra* is 483% and 335% relative to the control values. Characteristically, these species are prone to contain a greater amount of glutathione.

The smaller amount of this compound in the leaves of a plant such as *T. cordata* having a high sulfur-accumulating capacity under the conditions of significant atmospheric pollution (Zaporizhstal and Vohnetryv factories) can be explained by the inhibition of the inclusion of sulfur in the amino acid cysteine, which is a component of the tripeptide. A lower level of SO<sub>2</sub> emissions in the air around ZTMC causes a slight increase in the amount of glutathione in the leaves of plants of this species in relation to the control values.

The higher content of the tripeptide in the leaves of most plant species in the sanitary protection zones compared to our control values confirms the opinion of Kok (1986) on the possible protective role of this compound under the conditions of intoxication of plants by sulfur dioxide (SO<sub>2</sub>).

## Conclusions

The accumulation of sulfur in leaves of woody plants growing in conditions of outdoor air pollution by sulfur dioxide (SO<sub>2</sub>) occurs during the entire vegetation period, being the most intense in young leaves that have already finished growing. The maximum amount of element is detected at the end of the vegetation period.

The higher the level of pollutant emissions in the atmosphere of a given enterprise, the higher the concentration of sulfur in the leaves of woody plants in the sanitary protection zones of industrial enterprises but the degree of increase of the content of the pollutant in the leaves of plants of various protective plantations is not proportional to the quantitative indicators of the level of SO<sub>2</sub> in the air.

Woody plant species were divided into three groups according to the amount of sulfur accumulated in their leaves: I – the maximum level – *Betula pendula*, *Tilia cordata*, *Salix alba*, *Robinia pseudoacacia*, *Populus alba*, *Populus simonii*, *Populus nigra*, II – medium – *Acer platanoides*, *Acer negundo*, *Fraxinus lanceolata*, *Catalpa bignonioides*, III – the smallest – *Morus alba*, *Ailanthus altissima*, *Elaeagnus angustifolia* and *Ulmus carpinifolia*.

The increase of sulfur concentration in the leaves of woody plants growing in the areas of sanitary protection zones, in relation to the control parameters, is consistent with the increase in their content of glutathione, which is not only of an important physiological significance, but also its formation can be one of the ways of metabolizing this element.

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 a subsequent study, the accumulation of gaseous pollutants such as chlorine and phenol in the leaves of woody plants growing in and around protective forest belts will be examined.

## References

- Al-Jahdali, M. O., & Bin Bisher, A. S. (2008). Sulfur dioxide (SO<sub>2</sub>) accumulation in soil and plant's leaves around an oil refinery: A case study from Saudi Arabia. *American Journal of Environmental Sciences*, 4(1), 84–88.
- Baciak, M., Warminiński, K., & Bęś, A. (2015). The effect of selected gaseous air pollutants on woody plants. *Leśne Prace Badawcze*, 76(4), 401–409.
- Barahtenova, L. A. (1995). Vozdushnye polljutanty i obmen sery u sosny obyknovnoy, porogovyye koncentracii, jeffekty zashhity [Air pollutants and gaseous exchange of sulfur of a Scots pine tree, threshold concentrations, impact of protective measures]. *Contemporary Problems of Ecology*, 1995(6), 478–494 (in Russian).
- Basovic, M., Prica, V., Velagic-Habul, E., & Bogdanovic, Z. (1975). Absorption sposobnosti listanekih listopadnih parkovchih kultura za SO<sub>2</sub> u aerozagadennoj sredini. *Golišn Biological Institute, Univerzitet u Sarajevu*, 28, 29–38.
- Bessonova, V. P. (1993). Jefferktivnost' osazhdeniya pylevyh chastic list'jami drevnyh i kustamyh rastenij [Efficacy of deposition of dust particles by leaves of shrubs and woody plants]. In: Oleksienko, T. D. (Ed.). *Voprosy zashhity prirodnoj sredy i ohrany truda v promyshlennosti. Dnepropetrovskij Gosudarstvennyj Universitet, Dnepropetrovsk*. Pp. 34–37 (in Russian).
- Bessonova, V. P., & Zajceva, I. A. (2008). Vmest vazhkyh metaliv u lysti drev i chagamykiv v umovah tehnogennogo zabrudnennja riznoy pohodzhennja [The content of heavy metals in the leaves of trees and shrubs under the conditions of man-made pollution of various origins]. *Problems of Bioindications and Ecology*, 13(2), 62–77 (in Ukrainian).
- Brandle, K., & Schnyder, J. (1970). Abtransport von schwefelverbindungen as bohenprimärfblättern (*Phaseolus vulg.*) nach begasung mit H<sub>2</sub>S. *Experimentia*, 26, 112–123.
- Bytnerowicz, A., Olszyk, D. M., Kats, G., Dawson, P. J., Wolf, J., & Thompson, C. R. (1987). Effects of SO<sub>2</sub> on physiology, elemental content and injury development of winter wheat. *Agriculture, Ecosystems and Environment*, 20(1), 37–47.
- Cicek, A., & Koparal, A. S. (2004). Accumulation of sulfur and heavy metals in soil and tree leaves sampled from the surroundings of Tuncbilek Thermal Power Plant. *Chemosphere*, 57(8), 1031–1036.
- Comish, L. (1968). Contribution à l'étude de l'absorption du soufre du dioxyde de soufre. *Annals of Physiology Vegetable*, 10(2), 99–112.
- Faly, L. L., Kolombar, T. M., Prokopenko, E. V., Pakhomov, O. Y., & Brygadyrenko, V. V. (2017). Structure of litter macrofauna communities in poplar plantations in an urban ecosystem in Ukraine. *Biosystems Diversity*, 25(1), 29–38.

- Fried, M. (1949). The absorption of sulphur dioxide by plants as shown by the use of radioactive sulphur. *Proceedings of the Soil Science Society of America*, 13(2), 135–138.
- Getko, N. V. (1989). Rastenija v tehnogennoj srede [Plants in an industrial environment]. Nauka i Tehnika, Minsk (in Russian).
- Godzik, S. (1976). Pobieranie  $^{35}\text{SO}_2$  powietrza i rozmieszczenie  $^{35}\text{S}$  u niektórych gatunków roślin. *Badania porównawcze. Instytut Podstaw Inżynierii Środowiska Polskiej Akademii Nauk*, 16, 159.
- Guderian, R. (1979). *Zagryaznenie vozdukhnoy sredy* [Air pollution]. Mir, Moscow (in Russian).
- Heber, U., & Hüve, K. (1997). Action of  $\text{SO}_2$  on plants and metabolic detoxification of  $\text{SO}_2$ . *International Review of Cytology*, 177, 255–286.
- Hijano, C. F., Domínguez, M. D., Giménez, R. G., Sánchez, P. H., & García, I. S. (2005). Higher plants as bioindicators of sulphur dioxide emissions in urban environments. *Environmental Monitoring and Assessment*, 111, 75–88.
- Hock, N. B., & Anderson, J. N. (1978). Chloroplast cysteine syntheses of *Trifolium repens* and *Pisum sativum*. *Photochemistry*, 17(5), 879–885.
- Hwangbo, J. K., Lee, C. S., & Kim, J. H. (2000). Tolerance of several woody plants to sulphur dioxide. *Korean Journal of Biological Sciences*, 4(4), 337–340.
- Iľkun, G. M., & Morgun, V. V. (1980). Pogloshhenie i vydelenie ionov kornjami rastenij v zagryaznennoj atmosfere [The absorption and release of ions by the roots of plants in a polluted atmosphere]. *Fiziologija Rastenij*, 27(1), 150–156 (in Russian).
- Iľkun, G. V. (1978). *Zagryazniteli atmosfery i rastenija* [Plants and outdoor air pollutants]. Naukova Dumka, Kiev (in Russian).
- Kaljužnyj, D. N. (1981). Sanitarnaja ohrana atmosfernogo vozduha ot vybrosov predpriyatij chernoj metalurgii [Sanitary protective measures with regard to atmospheric air and its pollution by emissions of the enterprises of ferrous metallurgy industry]. Gosmedizdat, Kiev (in Russian).
- Kapeljush, N. V., & Bessonova, V. P. (2007). Seredochishhuval'na rol' *Platanus orientalis* u nasadzhennjah sanitarno-gigijenichnogo pryznachennja [The role of *Platanus orientalis* in sanitary and hygienic plantations as a universal biofilter]. *Visnyk of Dnipropetrovsk University, Biology, Ecology*, 15(1), 59–66 (in Ukrainian).
- Kok, L. J., Maas, F. M., Godeke, J., Haaksma, A. B., & Kuiper, P. J. C. (1986). Glutathione, a tripeptide which may function as a temporary storage compound of excessive reduced sulphur in  $\text{H}_2\text{S}$  fumigated spinach plants. *Plant and Soil*, 91(3), 349–352.
- Korshikov, I. I., Kotov, B. C., Miheenko, I. P., Ignatenko, A. A., & Chernysheva, L. V. (1995). Vzaimodejstvie rastenij s tehnogenno zagryaznennoj sredoj. [Plant - environment interactions under the conditions of man-made pollution]. Naukova Dumka, Kiev (in Russian).
- Kozjukina, Z. T., Mihajlov, O. F., Miljan, M. N., & Moroz, N. I. (1980). Rol' rastenij v biologicheskoy chistke atmosfery ot letuchih toksikantov [The role of plants in the biological purification of atmosphere from volatile toxicants]. In: *Gazoustojchivost' Rastenij*. Nauka, Novosibirsk. Pp. 179–180 (in Russian).
- Kulagin, J. Z. (1970). Gazoustojchivost' drevesnyh rastenij i nakoplenie sery v ih list'jah [Gas resistance of woody plants and sulfur accumulation in their leaves]. In: Kolesnikov, B. P., & Mamaev, S. A. (Eds.). *Rastitel'nost' i Promyshlennye Zagryaznenija*. Ural'skij Gosudarstvennyj Universitet, Sverdlovsk. Pp. 36–41 (in Russian).
- Li, Z. G., Min, X., & Zhou, Z. H. (2016). Hydrogen sulfide: A signal molecule in plant cross-adaptation. *Frontiers in Plant Science*, 26(7), 1–12.
- Likus-Cieslik, J., & Pietrzykowski, M. (2017). Vegetation development and nutrients supply of trees in habitats with high sulfur concentration in reclaimed former sulfur mines Jeziorko (Southern Poland). *Environmental Science and Pollution Research International*, 24(25), 20556–20566.
- Liu, Y., Zhang, Y., Li, C., Bai, Y., Zhang, D., Xue, C., & Liu, G. (2018). Air pollutant emissions and mitigation potential through the adoption of semi-coke coals and improved heating stoves: Field evaluation of a pilot intervention program in rural China. *Environmental Pollution*, 240, 661–669.
- Madamanchi, N. R., & Alscher, R. G. (1991). Metabolic bases for differences in sensitivity of two pea cultivars to sulfur dioxide. *Journal of Plant Physiology*, 97, 88–93.
- Malhotra, S. S., & Hocking, D. (1976). Biochemical and cytological effects of sulphur dioxide on plant metabolism. *New Phytologist*, 76(2), 227–237.
- Martynov, V. O., & Brygadyrenko, V. V. (2017). The influence of synthetic food additives and surfactants on the body weight of larvae of *Tenebrio molitor* (Coleoptera, Tenebrionidae). *Biosystems Diversity*, 25(3), 236–242.
- Mitchell, R., Maher, B. A., & Kinnersley, R. (2010). Rates of particulate pollution deposition onto leaf surfaces: Temporal and inter-species analyses. *Environmental Pollution*, 58(5), 1472–1480.
- Mochalova, A. D. (1975). Spektrofotometricheskij metod opredelenija sery v rastenijah [Spectrophotometric method for the determination of sulfur content in plants]. *Sel'skoe Hozjajstvo za Rubezhom*, 4, 17–27 (in Russian).
- Nikolaev, G. V. (1963). Peredvizhenie fosfora, kal'cija i sery ot odnih rastenij k drugim cherez ih kornevye vydelenija [Translocation of phosphorus, calcium and sulfur from one plant to another by means of root excretions]. *Fiziologija Rastenij*, 10(4), 441–447 (in Russian).
- Okpodu, C. M., Alscher, R. G., Grabau, E. A., & Cramer, C. L. (1996). Physiological, biochemical and molecular effects of sulfur dioxide author links open overlay panel. *Journal of Plant Physiology*, 148(3–4), 309–316.
- Paul, R. (1974). L'absorption foliaire Le dioxyde De soufre atmospherique et son utilisation eventuelle par la plante. *Annual Gembloux*, 80(2), 95–103.
- Paul, R. (1976). Translocation du soufre d'origine atmospherique dans la plante. *Bulletin de la Société Royale de Botanique de Belgique*, 109(1), 13–23.
- Pöykiö, R., & Torvela, H. (2001). Pine needles (*Pinus sylvestris* L.) as a bioindicator of sulphur and heavy metal deposition in the area around a pulp and paper mill complex at Kemi, Northern Finland. *International Journal of Environmental Analytical Chemistry*, 79, 143–154.
- Roberts, B. R. (1974). Foliar sorption of atmospheric sulfur dioxide by woody plants. *Environmental Pollution*, 7(2), 133–140.
- Schiff, J. A., & Hodson, R. C. (1973). The metabolism of sulfate. *Annual Review of Plant Biology*, 24, 381–414.
- Sergejchik, S. A. (1997). Rastenija i jekologija [Ecology and plants]. Uradszhaj, Minsk (in Russian).
- Sergejchik, S. A., Sergejchik, A. A., & Sidorovich, E. A. (1998). Jekologicheskaja fiziologija hvoynyh porod Belarusi v tehnogennoj srede [Environmental physiology of coniferous plants of Belarus in a technogenic environment]. *Belaruskaja Nauka*, Minsk (in Russian).
- Simon, E., Braun, M., Vidie, A., Boggio, D., Fabian, I., & Tothemérsz, B. (2011). Air pollution assesment based on elemental concentration of leaves tissue and foliage dust along an urbanization gradient in Vienna. *Environmental Pollution*, 159, 1229–1233.
- Smit, U. H. (1985). Les i atmosfera: Vzaimodejstvie mezhdu lesnymi ekosistemami i primesjami atmosfernogo vozduha [Atmosphere and forest: Interactions between forest ecosystems and impurities in the outdoor air]. Progres, Moscow (in Russian).
- Stratu, A., Costică, N., & Costică, M. (2016). Wooden species in the urban green areas and their role in improving the quality of the environment. *Present Environment and Sustainable Development*, 10(2), 173–184.
- Subba, J. R., Thammakhet, C., Thavarungkul, P., & Kanatharana, P. (2016). Distributions of  $\text{SO}_2$  and  $\text{NO}_2$  in the lower atmosphere of an industrial area in Bhutan. *Journal of Environmental Science and Health, Part A*, 51(14), 1278–1288.
- Tarabrin, V. P., Chernyshova, L. V., Makogonov, B. C., & Honahbaev, V. N. (1971). Povrezhdenie rastenij semistym angidridom [Sulfur anhydride damage to plants]. *Rastitel'nost' i Promyshlennaja Sreda*. Naukova Dumka, Kiev. Pp. 21–29 (in Russian).
- Tarabrin, V. P., Kondratjuk, V. N., & Bashkatov, V. T. (1986). Fitotoksichnost' organicheskikh i neorganicheskikh zagryaznitelej [Phytotoxicity of organic and inorganic pollutants]. Naukova Dumka, Kiev (in Russian).
- Tripodo, P., Andelini, R., Mazzoleni, S., & Nanes, F. (1992). Foliar peroxidase activity and sulfate content as indicators of the urban pollution climate. *Annals of Botany*, 50, 49–61.
- Tuygun, G. T., Altuğ, H., Elbir, T., & Gaga, E. E. (2017). Modeling of air pollutant concentrations in an industrial region of Turkey. *Environmental Science and Pollution Research International*, 24(9), 8230–8241.
- Vasfilov, S. P. (2013). Dinamika soderzhanija sery v list'jah berezy v hode vegetacii v uslovijah zagryaznenija vozduha [Dynamics of sulfur content in birch leaves during the vegetation period under the conditions of air pollution]. *UT Research Journal. Natural Resource Use and Ecology*, 12, 103–111 (in Russian).
- Zhang, X., Zhou, P., Zhang, W., Zhang, W., & Wang, Y. (2013). Selection of landscape tree species of tolerant to sulfur dioxide pollution in Subtropical China. *Open Journal of Forestry*, 3(4), 104–108.