Biochemical indicators of woody plants in the diagnosis of air condition

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Abstract. It is found that anthropogenic pollution has a significant effect on the change in the content of total nitrogen, glutathione and vitamin E, which increases the resistance of woody plants to stress. A series of woody plants with regard to their sensitivity to aerosol pollution has been compiled: according to the degree of decrease in total nitrogen – Picea abies > Thuja occidentalis > Syringa vulgaris > Acer platanoides > Tilia cordata > Sorbus aucuparia; the degree of decrease in glutathione content – Picea abies > Thuja occidentalis > Syringa vulgaris > Acer platanoides > Tilia cordata > Sorbus aucuparia; the degree of decrease in the content of vitamin E – Picea abies > Thuja occidentalis > Sorbus aucuparia > Tilia cordata > Syringa vulgaris > Acer platanoides. A positive correlation was revealed between the biochemical parameters of woody plants and the monitoring complex indices proposed by the Russian meteorological service. A close direct regression dependence of the air pollution index and the average stability coefficient for the content of total nitrogen, vitamin E and glutathione in the biomass of model woody plants was revealed: with an increase in the degree of air pollution, the average stability coefficient for certain biochemical indicators increases.

1. Introduction
The introduction of early diagnostics of the environmental state is one of the priority directions in the implementation of environmental programs in the biosphere in order to ensure the environmental safety of the population. A number of authors believe that the most sensitive biological parameters include biochemical indicators in which transformations are observed first in cells, while morphological, physiological and other deviations from the norm are not yet recorded [1]. Plant objects and their biochemical parameters, according to a number of authors, are referred to as the optimal bioindication test system that responds adequately and quickly to environmental pollution of anthropogenic etiology [2–4]. The most convenient in such studies are the biochemical parameters of woody plants; dendroflora is of particular interest, since, being a long-term stationary object, it is capable of long-term deposition of toxic pollution over a number of years. The universal protective properties of dendroflora in response to abiotic and technogenic factors include the activation of biochemical multifunctional antioxidant protection in the form of amino acids, their enzymes (proline, glutathione, peroxidase and others), an increase in the content of water-soluble (C, B1-B12 and others) and fat-soluble (E, D, A) vitamins, macronutrients (nitrogen, phosphorus, potassium), sugar dynamics [5–7]. Foreign authors, combining biochemical, morphological, anatomical, and physiological indicators of trees, use the air pollution tolerance index for the comparative characteristics of species,
indirect assessment of the air condition, comparative diagnostic measures [7-9]. The different tolerance of woody plants to general air pollution in urbanized landscapes allows not only the effective bioindication, but also using the eco-physiological reactions of species individuals in the design of protective green spaces, which determine the absorptive capacity of urban forests and the health of city dwellers [10–12].

2. Materials, methods and research techniques
The aim of this work is to represent biochemical indicators for woody plants in the Non-Black Earth Region of the Russian Federation as basic data for organizing air biomonitoring. For the first time, biochemical data for the subsequent analysis of the air condition were obtained for the Dyatkovo district of the Bryansk region as a territory with combined chemical and radionuclide pollution, significant anthropogenic load, having the highest pollution rates for a number of years [13]. Biochemical indicators – the content of nitrogen, glutathione, vitamin E – were determined for 6 background species of woody plants in 120 samples: Acer platanoides L., Tilia cordata Mill.; Picea abies (L.) Karst., Thuja occidentalis L., Sorbus aucuparia L., Syringa vulgaris L. Subsequently, the data on the content of these substances in the biomass of species will serve to develop an ecological and biological ‘air pollution index – tolerance index’, similar to the foreign one.

The following methods has been applied: full-scale and office, laboratory-chemical: the content of total nitrogen, glutathione, vitamin E [14]. The samples were taken on the territory of 11 settlements, including the township of Kletnya (baseline data).

3. Results and Discussion
The instrumental studies have shown that in 2020 the dirtiest atmospheric air was recorded in the following settlements: Dyatkovo town, Berezino village, Lyubokhna township, Star’ township and Ivot township. The air pollution index (API) ranged within 7.646–5.01 (enhanced level), the average API value was 5.29 (figure 1).

![Figure 1](image_url)

**Figure 1.** Index of air pollution (API) in the Dyatkovo district (in 2020). Settlements (NP). 1 – the township of Bytosh, 2 – the town of Dyatkovo, 3 – the township of Ivot, 4 – the township of Lyubokhna, 5 – the township of Star’, 6 – the village of Berezino, 7 – Druzhba settlement, 8 – the village of Verkhi, 9 – the village of Nemerichi, 10 – the village of Slobodishche, 11 – the reference area (the village of Kletnya, Kletnyansky district).
Other, An excess of Maximal Admissible Concentrations (MAK) was recorded as follows: for nitric oxide (II) – a 1.070–2.421-fold increase (for nitrogen dioxide – a 1.020–1.304-fold increase, for formaldehyde – a 1.101–2.283-fold increase, for sulfur dioxide – a 1.050–3.480-fold increase, for hydrogen sulfide – a 1.372–1.024-fold increase, for carbon monoxide – a 1.080–2.902-fold increase, for ammonia – a 1.153–1.750-fold increase. The results of sampling in the settlements of the Dyatkovo district showed the exceedance in the reference area (the township of Kletnya): for nitric oxide (II) – a 0.384–24.180-fold increase, for nitrogen dioxide – a 1.200–1.550-fold increase, for sulfur dioxide – a 1.854–4.010-fold increase, for carbon monoxide – a 1.472–4.850-fold increase, for ammonia – a 1.801–3.890-fold increase. Formaldehyde and hydrogen sulphide were not recorded in the reference area, so no comparison was made with regard to these substances.

Based on the results of laboratory chemical studies, a series of sensitivity of woody plants to aerosol pollution was compiled according to the degree of decrease in the total nitrogen content in biomass (for example, the town of Dyatkovo): Picea abies > Thuja occidentalis > Syringa vulgaris > Acer platanoides > Tilia cordata > Sorbus aucuparia. Similar tendencies were observed for plants from other settlements of the Dyatkovo district.

It is important to note that in relatively clean (reference area) conditions, it is difficult to track the sensitivity of plants to aerosol pollution due to their low concentration or their absence.

The obtained spectrum of the phytotarium showed that conifers are the most sensitive to aerosol contamination as compared to deciduous ones. Most likely, plants exhibit species-specific response to the same aerosol pollutants, which is associated with their physiological characteristics.

Figures 2–3 show the average stability coefficients (SC) of dendroflora (according to the content of total nitrogen, glutathione, vitamin E).

![Figure 2. Average coefficient of stability (A – according to the content of total nitrogen; B – according to the content of glutathione, mg% per wet weight) of plant biomass in the Dyatkovsky district. Settlements. 1 – the town of Dyatkovo, 2 – the village of Berezino, 3 – the township of Lyubokhna, 4 – the township of Bytosh, 5 – the township of Star’, 6 – the township of Ivot, 7 – the village of Nemerichi, 8 – the village of Druzhba, 9 – the village of Verkhi, 10 – the village of Slobodishche.](image-url)

A series has been compiled according to the loss of stability coefficient with regard to the content of total nitrogen in woody plants: Dyatkovo> Berezino> Lyubokhna> Star> Ivot> Druzhba> Verkhi> Nemerichi> Slobodishche. The research findings showed that the content of total nitrogen in the leaves of some woody plants in 6 settlements of the district (Dyatkovo, Berezino, Lyubokhna, Star’, Ivot) is verifiable and 1.32–1.21 times higher than in the reference area (t measured> t tabular, P = 99.0%). In the other four settlements, this exceedance is not verifiable (t measured< t tabular). A series of woody plants sensitive to aerosolization is revealed according to the degree of decrease in glutathione, and, consequently, an increase in resistance to stress of this dendroflora: Picea abies > Thuja occidentalis > Syringa vulgaris > Acer platanoides > Tilia cordata > Sorbus aucuparia. The
series has been compiled according to the reduction of stability coefficient in terms of the content of glutathione in woody plants: Dyatkovo > Berezino > Lyubokhna > Star’ > Ivot > Druzhba > Verkhi > Nemerichi > Slobodishche. The coefficient of stability increases with an increase in aerosol pollution. The research findings showed that the content of glutathione in the phytomass of some woody plants in six settlements of the area (Dyatkovo, Berezino, Lyubokhna, Star’, Ivot) is verifiable and 1.20–1.37 times higher than in the reference area (t measured > t tabular, P = 99.0%). In the other four settlements, this excess is invalid (t measured < t tabular). Studies have shown that the content of vitamin E naturally increases with increasing air pollution. A series is revealed in terms of the decrease in the content of vitamin E in plant leaves, and, consequently, an increase in resistance to stress: Picea abies > Thuja occidentalis > Sorbus aucuparia > Tilia cordata > Syringa vulgaris > Acer platanoides.

Figure 3. Average coefficient of stability in terms of vitamin E content (mg% per wet weight) of plant biomass in the Dyatkovo district. The name of the settlements corresponds to the designations in Figure 1.

Compared to the reference area, the stability coefficient with regard to vitamin E content in the Dyatkovo district (t measured > t tabular, P = 99.0%) has a reliable 0.61-2.30-fold difference only in the following settlements: Dyatkovo, Berezino, Lyubokhna, Star’, Ivot. A positive feedback was revealed between the biochemical parameters of woody plants and the monitoring complex indices proposed by the Russian meteorological service. Figure 4 shows the regression dependence of the air pollution index (API) and the average stability coefficient for the total nitrogen content in the biomass in the Dyatkovo district. There is a direct dependence between the parameters: with an increase in the degree of pollution, the average stability coefficient depending on the content of total nitrogen in the biomass of model trees grows. The value of the approximation reliability amounted to 0.9072, which indicates a positive correlation between the parameters (F measured > F tabular).
Figure 4. Regression dependence of API and the average stability coefficient (SC) depending on the content of total nitrogen in biomass in the Dyatkovo district (as of 2020).

Figure 5 shows the regression dependence of API and average SC depending on the content of glutathione in the biomass of woody plants in the Dyatkovo district. The direct relationship between the parameters indicates that with an increase in the degree of pollution, the average SC for the content of glutathione in the biomass increases. The value of the approximation reliability amounted to 0.8478, which indicates a positive correlation between the parameters (F measured > F tabular).

Figure 5. Regression dependence of API and average stability coefficient for the content of glutathione in biomass in the Dyatkovo district (as of 2020).

Figure 6 shows the regression dependence of API and average SC for the content of vitamin E in biomass in the Dyatkovo district.
Figure 6. Regression dependence of API and average stability coefficient for the content of vitamin E in biomass in the Dyatkovo district (as of 2020).

The direct relationship between the parameters confirms the following tendency: the average SC for the content of vitamin E in biomass grows as the degree of pollution increases. The value of the approximation reliability amounted to 0.7102, which indicates a positive correlation between the parameters (F measured > F tabular).

4. Conclusion
The research findings showed that woody plants are significantly affected by air pollution. Under the experimental conditions in the Non-Black Earth Region of the Russian Federation, an increase in the content of nitrogen, glutathione, vitamin E is observed in plants. This happens with an increase in atmospheric air pollution. The biochemical data obtained and presented for the first time for the conditions of the old-developed region are in adequate agreement with the instrumental results and annually calculated pollution indices. It is recommended to use biochemical parameters of woody plants in biomonitoring, and to take into account the revealed resistance spectra of dendroflora in comparative studies. Conifers have shown the highest sensitivity to pollution in the studies.

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