The Accumulation of Heavy Metals in the Leaves of *Crataegus Sanguinea* Pall. (Redhaw Hawthorn) in the Urban Environment (On the Example of Orenburg)

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Abstract. Trees growing in the city play an essential role in cleaning the atmosphere from various pollutants. We investigated the possibility of using *Crataegus sanguinea* Pall. (Redhaw hawthorn) as a bioindicator of air pollution with heavy metals and toxic elements in Orenburg. We analyzed the impact of air pollution by evaluating the morphometric parameters and chemical properties of redhaw hawthorn leaves. Redhaw hawthorn leaves were collected in the areas with the most anthropogenic stress. We compared the amount of cadmium, copper, lead, zinc, and iron in the leaves. The plants in urbanized areas accumulated more heavy metals than the control samples. We organized heavy metals in a descending list by the intensity of their accumulation in plants: lead > copper > iron > zinc > cadmium. Our study demonstrated that redhaw hawthorn could be used as a pollution indicator in urbanized areas. Biomonitoring can be used to assess environmental pollution and rationally manage the environment in urban areas.

Keywords: *Crataegus sanguinea* Pall. · Accumulation · Bioindication · Heavy metals · Leaf area

1. Introduction

The ecological factors in urbanized areas differ from those in the natural environment. Due to the high surface area, plants are susceptible to environmental pollution. Through their contact area with the environment, plants absorb not only vital substances but also various pollutants. The absorption capacity is exceptionally high in leaves. Considerable amounts of dust particles and pollutants can settle on the surface of leaves and penetrate it via stomata [7, 9, 12, 11].

The absorbed pollutants accumulate in the cells and tissues of a plant, significantly affecting its physiological state and morphology. In this respect, perennial trees and shrubs are more vulnerable because toxic substances can continuously accumulate in the body for several years. The accumulation of substances harmful to the plant also affects the growing season. This often manifests itself in a shifting of plant life-cycle stages (e.g., earlier yellowing and falling of leaves resulting in a reduction of the growing season). Some pollutants may cause stomatal “paralysis” - a condition when the plant loses the ability to regulate stomata. Stomata become wide open, which disrupts the intra-plant water cycle and leads to a faster moisture loss.

Heavy metals form a special type of pollutants that harm the plant. However, some heavy metals are present in plants in small amounts to ensure their vital activity [14]. Nevertheless, an increased concentration of these metals negatively affects the plant. Exceeding the maximum concentration can form development abnormalities in the plant or even kill it [10].
Metals can influence the life processes of plants in different ways. For example, an increase in cadmium and zinc content inhibits cell growth. The accumulation of lead causes abnormalities in mitotic processes, stumping the plant’s growth. Additionally, some metals can replace the elements of the enzyme system in the plant, disrupting its work [13].

One of the primary sources of urban pollution is road transport. Heavy metals can enter the environment via vehicle emissions and asphalt abrasion. This way, such as zinc, nickel, lead, aluminum, cadmium, iron, and some other chemicals enter ecosystems. The most toxic of these are lead and cadmium [13].

Among the measures of monitoring the ecological situation, one of the most important is phytotesting. It is a system of biotesting, where vascular plants are used as the primary indicators. The study aims to identify variability in the accumulation of heavy metals by plants of the species *Crataegus sanguinea* Pall. (Redhaw hawthorn), growing along the car roads of Orenburg city.

2. Materials and Methods

Orenburg is a large city and the administrative center of the Orenburg Region, located in the Southern cis-Urals. The climate in the region is continental Dfa. In summer, the air humidity is low, precipitations are sparse, and the temperature is high. All of this causes periods of drought in the city. The climate also features low winter temperatures, and late-spring and early-fall frosts [3].

Orenburg Region is one of the most polluted ones in the Volga Federal District. In the last decade, the degree of air pollution in Orenburg was rated “high”, while the pollution index fluctuated between 5.1 and 8.8 units. Road transport is responsible for a significant amount of pollution. The amount of passenger cars increases every year - it more than doubled in size from 2000 to 2017.

This study examines *Crataegus sanguinea* Pall. – a perennial plant with high ecological plasticity. It is often used in greening landscaping of Orenburg. For the control group, we selected hawthorn plants growing on the territory of the Botanical Garden of Orenburg State University. The Botanical Garden is considerably far from major car roads; therefore, the plants are relatively unaffected by the immediate pollution.

The leaves were sampled at the end of the growing season. For the experimental groups, we sampled plants growing along heavy-traffic streets (Chicherina, Shevchenko, Turkestanskaya, Montazhnikov, Khabarovskyaya, Postnikova, Proletarskaya, and Tereshkova streets). These streets belong to four administrative districts of the city – Central (No. 1), Promyshlenny (No. 2), Leninsky (No. 3), and Dzerzhinsky (No. 4). The content of heavy metals was analyzed in the test lab of State Center for Agrochemical Service “Orenburgsky” using the AAS-4 Spectrophotometer. We analyzed the content of 5 metals (Cu, Zn, Pb, Fe, Cd), two of which (Pb, Cd) are highly toxic.

Leaf surface area was determined using the gravimetric method modified by L. V. Dorogan [4].

For a more precise assessment of the accumulation of heavy metals in the leaves, we used the concentration index of an element and the total concentration index of heavy metals [15]. The statistical data was processed in Microsoft Excel and Statistica 6.0.

3. Results

*Crataegus sanguinea* Pall. is a bushy tree that quite often grows in urban environments. Its leaves are oblong or broadly rhombic, with a sharp tip, wedge-shaped base, and serrated edges. The leaves of the plant have sparse trichome coverings. The adaxial surface is dark green; the abaxial is much lighter.

When collecting the biomaterial, we noted a significant number of damaged leaves. The leaves were affected with chlorosis and necrosis; the latter was observed at the top of the leaf, along the edges, and between the veins. To conduct the biochemical analysis and morphometric measurements, we needed to collect intact leaf samples. Therefore, the sampling was somewhat tricky and took much time.

The biochemical analysis results have shown that the control group did not necessarily have less heavy metals than the experimental groups. Some content indexes were higher than in the leaves
sampled from the urban environment. For example, cadmium content was higher in the control group. However, one must account for the leaf surface area (see table 1).

**Table 1. Heavy metals in the leaves of Crataegus sanguinea.**

| Sampling area | Leaf area, cm² | Cu          | Zn          | Pb          | Fe         | Cd          |
|---------------|----------------|-------------|-------------|-------------|------------|-------------|
| No. 1         | 27.44          | 1.85±0.55   | 14.2±6.2    | 0.095±0.005 | 60.5±10.4  | 0.052±0.023 |
| No. 2         | 30.69          | 2.25±0.35   | 8.8±0.6     | 0.23±0.12   | 65.9±7.1   | 0.028±0.01  |
| No. 3         | 31.30          | 2.75±0.35   | 9.45±0.45   | 0.27±0.18   | 65.75±3.65 | 0.042±0.003 |
| No. 4         | 29.33          | 3.25±0.25   | 15.55±3.55  | 0.05±0.01   | 56.6±5.3   | 0.079±0.011 |
| City average  | 29.69          | 2.53±0.47   | 12.0±2.87   | 0.16±0.08   | 62.4±3.9   | 0.05±0.015  |
| Control       | 40.20          | 1.8±0.4     | 17.4±3.6    | 0.058±0.02  | 50.6±10.7  | 0.055±0.19  |

*Source:* Compiled by the authors.

4. **Discussion**

Environmental pollution negatively affects the morphometric parameters of plants [1]. Under the influence of pollutants, the leaf surface area decreases. We noted a significant variation in leaf surface area between the studied samples. The control group had the largest leaf area – 40.2 cm². In urban samples, the index was lower, averaging at 29.7 cm². Since leaf surface areas varied significantly between the samples, we calculated the content of heavy metals per unit of surface area, i.e., per 1 cm² (see figure 1). The accumulation in control samples was significantly lower than in all experimental samples.

![Zn](image1.png) ![Cu](image2.png) ![Pb](image3.png) ![Cd](image4.png) ![Fe](image5.png)

**Figure 1.** The content of heavy metals in the leaves of Crataegus sanguinea by 1 cm²: No. 1 – Central district, No. 2 – Industrial, No. 3 – Leninsky, No. 4 – Dzerzhinsky, C – control. *Source:* Compiled by the authors.
We calculated the pollution indexes by the districts of the city and arranged them in descending order: Leninsky > Industrial > Dzerzhinsky > Central.

Having considered the average pollution indexes in the city, we arranged the heavy metals in descending order by their concentration in *Crataegus sanguinea* leaves: Pb > Cu > Fe > Zn > Cd.

All urban samples had high iron content. The adaptation mechanisms of the plants most likely cause this. Iron is essential for respiration and photosynthesis. By accumulating in large amounts, plants try to normalize vital metabolic processes in harsh environmental conditions.

To establish the correlation between the accumulation of two elements, we statistically processed the data using the Spearson correlation coefficient. The statistical analysis revealed a strong positive correlation between zinc and cadmium (r=0.9), and a strong negative correlation between cadmium and lead and cadmium and iron (r=-0.9) (see Table 2).

|       | Cu  | Zn  | Pb  | Fe  | Cd  |
|-------|-----|-----|-----|-----|-----|
| Cu    | r   | -0.3| 0.3 | 0.1 |
|       | $r_{\text{fact}}$ | -0.54| 0.54| 0.17|
|       | $r_{\text{theor}}$ | 3.04| 3.04| 3.04|
| Zn    | r   | -0.54| -2.31| -1  | 0.9 |
|       | $r_{\text{fact}}$ | -0.54| -2.31| -1  | 0.9 |
|       | $r_{\text{theor}}$ | 3.04| 3.04| 3.04|
| Pb    | r   | 0   | -0.8| 0.8 | -0.9|
|       | $r_{\text{fact}}$ | 0   | -2.31| -2.31| -3.56|
|       | $r_{\text{theor}}$ | 3.04| 3.04| 3.04|
| Fe    | r   | 0.54| 2.31| -3.56| -3.57|
|       | $r_{\text{fact}}$ | 0.54| 2.31| -3.56| -3.57|
|       | $r_{\text{theor}}$ | 3.04| 3.04| 3.04|
| Cd    | r   | 0.1 | 0.9 | -0.9| - |
|       | $r_{\text{fact}}$ | 0.17| 3.57| -3.56| -3.57|
|       | $r_{\text{theor}}$ | 3.04| 3.04| 3.04|

Source: Compiled by the authors.

We conclude that cadmium, iron, and lead are antagonists in this plant species, i.e., they inhibit each other's accumulation in the plant. Zinc is a chemical analog of cadmium, which can explain the positive correlation between them [2].

5. Conclusion
In this study, we analyzed the morphometric parameters of redhaw hawthorn leaves and the content of heavy metals in them. Moreover, we calculated pollution indexes and correlation coefficients of heavy metal accumulation. The control group significantly differed from urban samples by leaf surface area. The decreased leaf surface area in urban plants is caused by heavy technogenic stress and environmental pollution.

In the leaves of urban plants, the content of heavy metals was significantly higher than in the control group. Car emissions cause most environmental damage to the plants. The pollution indicators show that Leninsky district of Orenburg is mainly polluted by car emissions — the plants of this district had the highest amount of lead. High lead contents negatively affect the vital processes of plants and inhibit their viability in ecologically unfavorable conditions.

All the above proves the feasibility of using redhaw hawthorn as an indicator for monitoring the ecology of urbanized areas. Further studies in this field will be aimed at expanding the range of investigated chemical pollutants and finding new indicator species.
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