Phytoremediation potential of woody flora in urban areas

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Abstract. The development of industry, heavy metal pollution has created serious environmental problems. A phytoremediation is a group of environmental cleaning technologies. Currently relevant is the identification of representatives of the woody flora typical of the region from the accumulation of pollutant metals. For the study, 13 sites located on the territory of sanitary protection zones of industrial enterprises of the city of Orenburg were selected. The content of heavy metals was determined in the soil and plant biomass selected from the sites. An analysis of the results shows the relationship between the concentration of heavy metals in soil and plants. The ability of plants to accumulate elements is assessed. Thus, Ulmus glabra accumulates Co from mobile soil forms in 7 reference sites, the leaves of the plant deposit Pb in 4 reference sites. Ulmus glabra accumulates nickel and copper in 4 studied areas. When analyzing individual plant species, the best potential accumulating abilities are (in decreasing order): Ulmus glabra Huds. > Acer negundo L. > Betula pendula Roth.

1. Introduction
The development of modern industry, heavy metal pollution led to a serious environmental problem. Phytoremediation is an effective method for the restoration of contaminated soils. Many plants absorbed by the roots of metals are transported to the aerial parts of plants. This transportation of metals from the root to the shoot is dangerous, as metals can move from stems to leaves, then when eaten by birds and small herbivorous mammals from the environment, as well as from carnivores and to the human chain. Understanding the mechanisms underlying the accumulation and detoxification of heavy metals in plants is one of the key points of phytoremediation [7]. The choice of plant phytoremediators is based on their ability to naturally accumulate heavy metals [2, 5].

This research aims to develop recommendations for the selection of plant-intermediaries from among the typical representatives of plants of local flora.

2. Materials and methods
2.1. Place of study and sampling
The study was conducted in Orenburg. This city is the administrative centre of the Orenburg region, a subject of the Russian Federation. The area of Orenburg is 259 km², with a population of 564443 people. The climate of Orenburg is sharply continental. Continental climate is most clearly manifested in the features of the temperature regime and insufficient atmospheric moisture. The soils of Orenburg are represented by chernozems, which have been preserved only in areas with residual natural vegetation (floodplain forests, forest park zones) and fragmented in wastelands and underutilized lands.

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For the study, 13 reference plots (Table 1) located on the territory of sanitary protection zones of industrial enterprises were selected.

| No. | Enterprise                                      | Coordinates       |
|-----|------------------------------------------------|-------------------|
|     |                                               | Latitude, N       |
| 1   | ZAO "Strela"                                   | 51.799644         |
| 2   | OJSC "Radiator"                                | 51.784695         |
| 3   | OJSC "Hydropress"                              | 51.802341         |
| 4   | OJSC RTI Plant and OJSC Silicate Plant         | 51.784230         |
| 5   | OJSC "Refrigeration Equipment Plant"           | 51.809762         |
| 6   | OJSC "Neftemaslozavod"                         | 51.825196         |
| 7   | OJSC "Plant Spetselevatormelmash"              | 51.776634         |
| 8   | OJSC "Plant Inverter"                          | 51.811309         |
| 9   | OJSC Forshhtad                                 | 51.770131         |
| 10  | OJSC "Plant sanitary ware"                     | 51.806592         |
| 11  | OJSC Orenburgselkhozremont                     | 51.823292         |
| 12  | OJSC "Rembyttekhnika"                          | 51.825005         |
| 13  | OJSC Diesel Locomotive Repair Plant            | 51.786454         |

2.2. Sample preparation of soil samples
Point samples were taken using the “envelope” method (the length of the side of the square was 2 to 10 m, each sample was a part of the soil type of the studied soil horizons. Samples were collected from a depth of 0–10 cm. Five samples were taken from each point of the controlled area. The soil was examined for the gross content of heavy metals and mobile forms, using the atomic absorption method.

2.3. Plants as objects of study
Plant samples were collected during the growing season. Plants were examined on eight elements with an atomic absorption spectrophotometer. The leaves of 3 plant species from 3 families were analyzed, which are found everywhere in all areas of the study, except for Betulapendula Roth. Collection of Betulapendula Roth material produced in 2 reference plots. The investigated leaves of trees are sem. Aceraceaegus: Acer negundo L.; sem. Betulaceae s. F. Gray.: Betula pendula Roth.; Sem. Ulmaceaemirb.: Ulmus glabra Huds.

2.4. Determination of heavy metals
The determination of the heavy metals in the samples was conducted by atomic absorption spectrophotometry (AAS). A Thermo Scientific AAS Model iCE 3000 was used for quantitative analysis of the heavy metals in the samples. The quantitative analysis involved measuring the absorbance of each analyte in the samples and standard solutions. Lead, cadmium, copper, iron and zinc absorbances were measured at wavelengths of 283.3, 228.8, 324.7, 248.3 and 213.9 nm, respectively. A series of calibration standards were run in the AAS, and the calibration curves were used for calculation of the concentrations of the metals. The blank readings were subtracted from the sample readings [8].

The results obtained were subjected to statistical processing. Correlation analysis was performed by calculating the partial correlation coefficients for pairs of traits in all possible combinations with subsequent correction of the obtained values taking into account the sample size (Pearson correction for the number of observations). In statistical procedures, the level of significance of hypotheses was considered the level that provides an error probability of less than 5 % (p <0.05).

3. Results and discussion
3.1. Heavy metals in the soil
At the first stage of the study, we decided to establish typical and specific features of pollution of urban soils of the city with pollutants, including depending on the proximity of various industrial enterprises of the city, highways and interchanges, shopping centres and residential areas (Table 2).
Table 2. Correlation analysis of the content of gross and mobile forms of heavy metals in the soils of the study sites

| Plot number | Ni   | Co   | Pb   | Cd   | Cr   | Zn   | Cu   |
|-------------|------|------|------|------|------|------|------|
| 1           | 0.21*| 0.13*| –0.007 | u/l  | 0.63*| –0.09*| 0.56* |
| 2           | 0.29*| –0.62*| 0.51* | u/l  | 0.12*| 0.77* | 0.36* |
| 3           | 0.66*| 0.11*| 0.68* | u/l  | 0.52*| 0.26* | 0.01* |
| 4           | 0.43*| –0.04*| 0.61* | u/l  | 0.76*| 0.04* | 0.05* |
| 5           | 0.58*| –0.28**| –0.59**| u/l  | 0.19**| –0.25**| 0.06** |
| 6           | 0.04**| –0.75**| 0.88* | u/l  | 0.65*| –0.47**| 0.77* |
| 7           | 0.45**| 0.71*| 0.32* | u/l  | –0.54**| –0.93**| 0.98** |
| 8           | –0.01*| –0.45**| 0.27* | u/l  | –0.05**| 0.38* | 0.29** |
| 9           | 0.36*| –0.74**| 0.27* | u/l  | –0.56**| 0.66* | 0.28* | 0.61* |
| 10          | 0.89**| –0.48**| 0.08**| u/l  | 0.81*| –0.55*| 0.94** |
| 11          | –0.32**| –0.85**| 0.95* | u/l  | 0.22*| 0.32* | –0.07** |
| 12          | –0.98**| –0.69**| 0.89**| u/l  | –0.55*| –0.68*| –0.93** |
| 13          | –0.34*| –0.85**| –0.62*| u/l  | –0.50*| –0.44*| 0.97** |

Designation: * p <0.05. ** p <0.01, n/a - the results are not valid.

Heavy metals are of natural or anthropogenic origin. Heavy metals of lithogenic origin have less bioavailability because soils are exposed to various influences, leaving only metals that exist in a very stable form [6]. The free form of heavy metals is most often of anthropogenic origin, occurs in the form of dust and is found in the surface layers of soils. Table 2 shows the results of the correlation analysis (Pearson) of the relationship between the gross and mobile forms of heavy metals.

For heavy metals, a strong correlation was observed between many metals in the soil (coefficients> 0.7). High values of the correlation coefficient Cu indicate the lithogenic origin of the element [1], [3]. High concentrations of Cr and Ni in soils are attributed to the elemental composition of soils [4], or specific industrial sources, such as metallization.

Mathematical processing of experimental data showed that the soils of the “Rembyttekhnika site have a high proportion of the mobile form of nickel (r² = 0.89, at p <0.01), chromium (r² = 0.81, at p <0.05) and (r² = 0.94, at p <0.01), and for the company Spetselevatormelmaskobalt Co (r² = 0.71, at p <0.05) and copper (r² = 0.98 at p <0.01).

Analysis of pollutant content in soils showed an increased Cu content in 4 reference areas: OJSC "Nefemaslozavod," OJSC "Spetselevatormel Mash Plant," OJSC "Rembyttekhnika," OJSC "Santekhzagotovok," and lead in 3 research areas: OJSC Nefemaslozavod, Thermal Locomotive Repair OJSC, OJSC "Plant sanitary ware."

High values of Cr are characterized by higher protection zones: OJSC "RTI," Silicate Plant and OJSC "Rembyttekhnika."

The described features of the content of heavy metals indicate the more anthropogenic origin of elements than lithogenic. The study did not reveal significant and persistent anomalies in the accumulation of metals in soils in the reference areas of the city of Orenburg.

3.2. Heavy metals in plants

According to the results of the study, among the studied plants, we can distinguish species that are prone to the accumulation of heavy metals.

The increased Co content was noted in the leaves of Ulmusglabra on the territory of the sanitary protection zones of the reference areas: OJSC "RTI," Silicate Plant, OJSC "Nefemaslozavod" and OJSC "Inverter Plant."

The increased nickel content was determined in the leaves of Betulapendula, which grows on the reference site of OJSC "Inverter Plant. " Since no excess Ni concentration was observed in the soils of the site; therefore, atmospheric transport with dust was the primary source of the element.
3.3. Accumulation of pollutants by plants

The next stage of the study is the analysis of the features of correlation and regression relationships, reflecting the relationship between the concentrations of metals in soils and plants, we will initially consider models without a specific accessory (Table 3).

| Plot number | Plant species | Ni    | Co    | Pb    | Cd    | Cr    | Zn    | Cu    |
|-------------|---------------|-------|-------|-------|-------|-------|-------|-------|
| 1           | Acernegundo   | 0.51* | 0.59* | −0.035| −0.14*| 0.53* | −0.55*| −0.25*|
|             | Ulmusglabra   | −0.92**| 0.96**| 0.65* | 0.97**| 0.01* | 0.56* | −0.63*|
| 2           | Acernegundo   | −0.62*| 0.39* | −0.92**| −0.97**| −0.97**| −0.86**| −0.97**|
|             | Ulmusglabra   | −0.65*| 0.25* | −0.92**| −0.58* | −0.88**| −0.85**| −0.82**|
| 3           | Acernegundo   | 0.43* | −1**  | −0.99*| −0.92**| −0.54* | −0.99**| −0.53*|
|             | Ulmusglabra   | 0.091*| −0.94**| 0.98* | −0.99 | −0.39 | −0.75 | 0.99**|
|             | Betulapendula | −0.63*| −0.84*| −0.85*| 0.93**| −0.33*| 0.47* | 0.25* |
| 4           | Acernegundo   | −0.80**| −0.4* | 0.61* | −0.91*| 0.14* | 0.59* | 0.30* |
|             | Ulmusglabra   | 1**  | 0.57* | 0.12* | −0.89*| 0.1*  | −0.76*| −0.95**|
| 5           | Acernegundo   | 0.58* | 0.64* | 0.57* | 0.16* | 0.26* | −0.99**| 0.94* |
|             | Ulmusglabra   | 0.98**| 0.99**| 0.34* | −0.3* | 0.91**| −0.18*| 0.003*|
| 6           | Acernegundo   | −0.29*| 0.99**| 0.08* | −0.19*| 0.04* | −0.04*| −0.5* |
|             | Ulmusglabra   | 0.41* | 0.97**| 0.03* | −0.001*| 0.52* | 0.32* | −0.02*|
| 7           | Acernegundo   | 0.91**| 0.56**| 0.23* | 0.76* | 0.76* | 0.98* |
|             | Ulmusglabra   | 0.99**| −0.73*| −0.86*| −0.19*| 0.98* | 0.98* | 0.48* |
|             | Acernegundo   | 0.92**| −0.86*| 0.66* | 0.69* | 0.97**| 0.57* | −0.78*|
| 8           | Ulmusglabra   | 0.51* | 0.96**| 0.87* | −0.33*| 0.22* | 0.16**| 0.76* |
|             | Betulapendula | 0.49* | −0.56**| 0.93**| 0.81* | 0.89* | 0.7*  | 0.99* |
| 9           | Acernegundo   | −0.92**| 0.84* | 0.41* | 0.12**| 0.23* | −0.13**| −0.55**|
|             | Ulmusglabra   | −0.71**| 0.97* | −0.22**| 0.99* | −0.07**| −0.19**| −0.81**|
| 10          | Acernegundo   | −0.57*| 0.64* | −0.78*| −0.98**| 0.75* | −0.84*| 0.14**|
|             | Ulmusglabra   | −0.36*| 0.78* | 0.97**| −0.98**| 0.91**| −0.92**| 0.24* |
| 11          | Acernegundo   | 0.19**| 0.75* | −0.17**| −0.99*| 0.68* | 0.56* | −0.47*|
|             | Ulmusglabra   | −0.62*| 0.99**| −0.04**| −0.99*| 0.16**| −0.59*| −0.99**|
| 12          | Acernegundo   | 0.55* | 0.38* | −0.31*| −1** | 0.99**| −0.62*| −0.66*|
|             | Ulmusglabra   | 0.95* | 0.65* | 0.28* | −1** | 0.54* | −0.65*| 0.76* |
| 13          | Acernegundo   | −0.82**| 0.84* | −0.96**| 0.99**| 0.91**| −0.92**| 0.91* |
|             | Ulmusglabra   | −0.55**| −0.74*| 0.84* | −0.02**| 0.04**| −0.97*| 0.97* |

Designation: * p <0.05, ** p <0.01

Table 3 shows the results of a correlation analysis of the content of mobile forms of heavy metals in soils and leaves of plants. An analysis of the results made it possible to identify the most “available” elements for plants: Co, Cr, and Cu. Moreover, the best ability to accumulate heavy metals are Ulmusglabra > Acernegundo > Betulapendula.

In leaves, Ulmusglabra plants accumulate Co well in 7 reference sites with a maximum value of $r^2 = 0.99$ (at $p <0.05$), Pb in 4 reference sites of $r^2 = 0.98$ (at $p <0.05$), Ni on one plot ($r^2 = 1$, at $p <0.01$) and Cu in 4 sections ($r^2 = 0.99$ at $p <0.05$).

As a result of the analysis, we can conclude that the most effective mediator is Ulmusglabra Huds. Due to the rare occurrence of Betulapendula Roth in Orenburg, it is not easy to talk about this plant as a phytoremediator. However, it can be assumed that this plant has a high remediation potential.

Thus, the analysis of the frequency and magnitude of excess metals in soils and plants does not indicate the presence of coincidences among pollutants, which were determined in high concentrations in soils and plants on the same reference sites. This fact is indirect evidence of the anthropogenic origin of pollutants.
4. Conclusions
The study did not reveal persistent anomalies in the accumulation of metals in soils in the reference areas of the sanitary protection zones of the city of Orenburg. No pronounced dominance of any pollutant was found either.

Assessment of the absolute concentration of heavy metals noted in soil and plant samples, the most “accessible” elements for plants should be distinguished: Co, Cr and Cu.

When analyzing individual plant species, the best potential accumulating abilities are Ulmusglabra > Acernegundo > Betulapendula.

Acknowledgments
The research was supported by the Ministry of Science and Higher Education in accordance with the state assignment for Ural State Mining University No. 0833-2020-0008 ‘Development and environmental and economic substantiation of the technology for reclamation of land disturbed by the mining and metallurgical complex based on reclamation materials and fertilizers of a new type’. We obtain the scientific results with the staff of Center for the collective use by using funds of the Center for the collective use of scientific equipment of the Federal Scientific Center of biological systems and agricultural technologies of RAS as well (No Ross RU.0001.21 PF59, the Unified Russian Register of Centers for Collective Use - http://www.ckp-rf.ru/ckp/77384).

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