Assessment of remediation potential of flora of the Southern Urals

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Abstract. Soil degradation caused by human activities currently remains one of the most important environmental problems. Phytoremediation is a group of technologies for environmental clean-up and soil restoration by plants. The level of soil contamination, the bioavailability of pollutants, as well as the accumulation of metals by the plant are crucial for phytoremediation. Currently, it seems relevant to study representatives of the herbaceous flora typical for the region from the point of view of accumulation of pollutant metals. For the study we selected 5 sites located in different areas of Orenburg city. The plots estimated the content of total and active forms of heavy metals in the soil. On the study sites, samples were taken from plants during the growing season. The study analyzed the biomass of 11 plant species from 5 families and 8 elements. As a result of a comparative analysis obtained, the paper presents calculated correlation coefficients (R) between the indicators of the concentration of heavy metals in the soil and plants from the point of view of the accumulation efficiency of Pb and Cd. Plants-phytoremediators accumulate Pb from inactive soil forms – Cichorium intybus L. (R²=0.72 at P<0.05) and Polygonum aviculare L. (R²=0.57 at P<0.05). Plant accumulating Pb due to the absorption of its active forms – Arctium lappa L. (R²= 0.4 at P<0.01). Promising phytoremediators of available forms of Cd – Polygonum aviculare L. (R²=0.65 at P<0.05) and Plantago media L. (R²=0.55  at P<0.05).

1. Introduction

The activity of the urban population leads to a sharp deterioration in the ecological qualities of the urban environment. The intensification of construction, increasing number of vehicles and the widespread use of artificial surfaces form a specific type of urban microclimate. We can see changed or destroyed soil cover [2, 17]. Specific soils or soil-like bodies are – urbanozem. Fears cause pollution of urban soils by pollutants, in particular heavy metals [9, 13, 14, 15]. Pollutants can leach out and move down the soil profile, all of which leads to pollution of groundwater and surface water [1, 2, 3, 5, 16]. Some metals and metalloids are physiologically necessary for all organisms as trace elements, but their high concentration in the soil has a harmful effect on the environment [1, 4, 7, 8, 20]. Thus, at present, soil pollution caused by human activities remains one of the most important environmental problems of urban ecosystems [11]. The solution to this problem is the development of new remediation technologies [9, 10, 12]. Remediation technologies are...
based on the use of plants (phytoremediators) for cleaning contaminated substrate from toxic metals and special agrotechnical techniques [13]. In the literature, phytoremediation can be as well as bioremediation or botanical one [3]. Phytoremediation is one of the most cost-effective ways to clean the soil, in contrast to traditional physico-chemical methods as in situ [7, 8, 11, 12]. The search for native plant species – hyper-accumulators and heavy metal remediation plants is relevant for urban and industrial areas at the global and regional levels.

The aim of our work is to develop recommendations on the choice of plants- remediators from among the typical representatives of the local flora based on an analysis of the relationship between the levels of pollution of urbanized soils and the grass growing on them. This is also the main task in the development of phytoremediation technologies.

2. Materials and methods

2.1 Place of study and sampling

The study was conducted in Orenburg city (Orenburg region, Russia) during 2008-2018 years. The area of Orenburg is 259 km² with a population of 564,443 people. The climate of Orenburg is sharply continental. The continentality of the climate is most clearly manifested in the features of the temperature regime, in the insufficiency and instability of atmospheric humidification. The soils of the city of Orenburg are black soils of Calcium Skeletal Black Soils according to IUSS Working Group WRB (2014). Soils are only in areas with residual natural vegetation (floodplain forests, forest-park zones) and fragmentary on wastelands and underutilized land mainly on the periphery of the city. Soils are characterized by a non-flushing water regime.

We selected 5 reference sites located in various micro districts of the city. (Table 1, fig. 1). The sites were located on the territory of industrial zones or at residential buildings.

| №  | Study site | Enterprise                           | Coordinates         |
|----|------------|--------------------------------------|---------------------|
| 1  | Industrial | OJSC «Gydropress»                     | 51°4813,2’ N 55°0336,7’ E |
| 2  |           | OJSC «Plant of Spetsmash»            | 51°4634,2’ N 55°0839,9’ E |
| 3  |           | OJSC «Plant Invertor»                | 51°4840,4’ N 55°0851,8’ E |
| 4  |           | OJSC «Forstadt» 60                   | 51°4630,9’ N 55°0848,9’ E |
| 5  |           | OJSC «Rembytehnika»                  | 51°4929,8’ N 55°0728,1’ E |
2.2. Sample preparation of soil samples
Point samples were selected by the “envelope” method (the length of the side of the square was equal to 2 to 10 m, each sample was a part of the soil typical of the soil horizons under study). Samples were collected from a depth of 0-10 cm. From each point of the site, 5 soil samples were taken. Soil samples were dried at $t = 20-25^\circ\text{C}$ and air humidity 50-60%, lumps were kneaded by hand and laid out in a dark dry place. Then quartz treatment was carried out, ¼ part was sieved with cells 1 mm in diameter. The soil was investigated for the content of total and active forms of heavy metals by the atomic absorption method.

2.3. Plants as objects of study
Collection of plant samples was carried out during the growing season. The plants were examined on 8 elements with an atomic absorption spectrophotometer. We conducted the analysis of 11 species of plants from 5 families, found everywhere in all areas of the study. Of these, 7 species of plants belonged to the Asteraceae dumort family (asteraceae). By 1 species of plants belonging to families: Papaveraceae Juss (papaveracea), Plantaginaceae Juss (plantaginaceae), Poaceae Barnhart (poaceae ), Polygonaceae Juss (polygonaceae). Based on the results of assessing the frequency of occurrence, species that are ubiquitous (in all studied areas of Orenburg city) were selected belonging to typical representatives of the regional flora: Elytrigia repens (L.) Nevski, Arctium lappa L., Chelidonium majus L., Cichorium intybus L., Plantago media L., Polygonum aviculare L., Taraxacum officinale Wigg., Artemisia absinthium L., Artemisia vulgaris L., Achillea millefolium L. Tanacetum vulgare L.

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
analysis in the samples and standard solutions. Lead, cadmium, copper, iron and zinc absorbance was measured at wavelengths of 283.3 nm, 228.8 nm, 324.7 nm, 248.3 nm and 213.9 nm, respectively. A series of calibration standards were conducted 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 [19]. The results were evaluated in terms of maximum permissible concentration (MPC) of metals in plants and soil.

The results were the subject of statistical analysis using the software package Statistica 8.0 for Windows. Correlation analysis was performed by calculating the partial correlation coefficients for pairs of signs in all possible combinations with the subsequent correction of the values obtained taking into account the sample size (Pearson's correction for the number of observations). In statistical procedures, the level of significance of hypotheses was the level that provides the probability of error less than 5% (P<0.05).

3. Results and discussion
For the study, 25 soil samples were taken from each reference area and 244 samples of above-ground parts of plants (from all areas). Samples of soil and plants were analyzed for Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. The overall structure of anthropogenic accumulation of toxic elements in the soil and plants is typical for large cities with industries in various sectors (fig. 2).

![Figure 2. The percentage of total and active forms of pollutants in the soils of Orenburg city](image)

The content of pollutants in the phytomass made it possible to identify the intensity of their accumulation and to develop models of the relationship between soil pollution and the accumulation of elements in plant organs.

3.1. Heavy metals in the soil
The selected soil samples of the city were characterized by a pH value ranging from neutral to slightly alkaline (6.8 - 8.1). Closeness to neutral reaction of the soil solution is due to the carbonate of the underlying...
rocks. Pollutants are accumulated by soil organic matter (mainly humic acids). Therefore, binding of heavy metal salts into stable complex compounds such as chelates occurs, translating them into an inaccessible (total) form for plants. Plants absorb only the water-soluble (active) part of the compounds. As a result, we have analyzed the active forms of pollutants in the soil and their relationship with plants.

3.2. Heavy metals in plants

When analyzing the concentrations of metals in the aerial parts of plants, we found that most of the pollutants in the study period have negative dynamics of accumulation. Depending on the effect of pollutants, we classified plants into categories:

1. Plants with constant (nearly constant) maximum permissible concentration (PCM) of pollutants (mainly Zn, Cr, Cd): Polygonum aviculare L.

2. Plants with frequent excesses of pollutants (Zn, Cr, Cd, Pb, Ni), for example: Cichorium intybus L., Plantago media L., Taraxacum officinale Wigg.

3. Plants that occasionally have significant concentrations recorded of PCM of pollutants: Elytrigia repens (L.) Nevski - Co, Cr, Ni, Zn, Pb, Arctium lappa L. - Co, Cr, Pb, Cd, Artemisia absinthium L. and Artemisia vulgaris L. - Cr, Ni, Zn, Pb, Cd, Achillea millefolium L. - Co, Cr, Zn, Pb).

Among the elements dominating in plants, Cr and Zn are noted, the levels of which either constantly or often exceeded the MPC during the entire observation period. Positive dynamics of metal concentrations in plants in all areas was observed for 3 years at Cichorium intybus L., Plantago media L. and Achillea millefolium L.

3.3. Accumulation of pollutants by plants

The next stage of the research was the analysis of the features of the correlation and regression links, reflecting the interrelation of the concentrations of metals in soils and plants, regardless of their species. Such an approach makes it possible to assess the ability of a chemical element to accumulate in the above-ground plant organs. Analyzing the absolute concentrations of heavy metals in soil and plant samples, the most “available” for plants elements were identified: Co and Cd. Regression models of the relationship of concentrations of heavy metals in soils and plants allowed us determine the effectiveness of their bio-adsorption (Table 2).

| Element | K | R   | K/MPC1 |
|---------|---|-----|--------|
| Pb      | 0.002 | 0.274² | 0.0003 |
| Cd      | 0.248 | 0.408³ | 0.6350² |
| Ni      | 0.074 | 0.171 | 0.0185 |
| Cr      | 0.212 | 0.240³ | 0.0353 |
| Zn      | 0.294 | 0.289³ | 0.0120 |
| Cu      | 0.228 | 0.371⁴ | 0.0760 |
| Co      | 0.405 | 0.358⁴ | 0.0810 |

Notes: K - regression coefficient; R - R; 1 - ratio of regression coefficient to MPC in soil; 2 - the ratio of the regression coefficient to the background (reference) values; 3 - P<0.05; 4 - P<0.01.

The values of the regression coefficients indicated the amount of the adsorbed chemical element in plants with an increase in the concentration of the element in the surface layers of the soil by 1 mg.
Comparison of the corresponding regression coefficients and MPC of chemical elements allowed them to be ranked in terms of ecological significance and indicated the greatest relevance of the phytoremediation model Cd (R=0.408 at P<0.01) (Table 2). As a result of statistical analysis, a positive significant correlation was found between the content of heavy metals (in mass and mobile forms) in the soil and in the phytomass of plants. Table 3 presents the averaged data of the correlation coefficients (R) of pollutants between the concentrations of metals in soils and above-ground organs of plants.

Table 3. Comparative analysis of the averaged data of the correlation coefficients (R) of pollutants from the point of view of plant utilization efficiency

| Pollutant | Total forms (R) | Active forms (R) |
|-----------|----------------|-----------------|
|          | Elytrigia repens | Arctium lappa L | Chelidonium majus L. | Cichorium intybus L. | Plantago media L. | Taraxacum officinale Wigg | Polygonum aviculare L. | Artemisia absinthium L. | Achillea millefolium L. |
| Pb       | -0.24           | -0.46           | 0.36             | 0.72               | -0.072            | 0.66               | 0.57               | 0.39               | -0.39             |
|          | 0.27            | 0.403           | 0.035            | 0.19               | 0.076             | -0.17              | 0.28               | -0.65              | 0.25             |
| Co       | 0.16            | 0.39            | 0.59             | 0.007              | 0.37              | -0.41              | 0.69               | 0.32               | -0.11            |
|          | -0.13           | -0.26           | -0.95            | 0.32               | -0.77             | 0.17               | 0.42               | -0.60              | 0.16             |
| Cu       | 0.09            | -0.98           | 0.12             | 0.49               | 0.32              | 0.14               | 0.05               | -0.33              | -0.59            |
|          | -0.28           | -0.45           | -0.26            | -0.036             | 0.079             | 0.12               | -0.07              | -0.31              | -0.45            |
| Cr       | -0.07           | 0.22            | -0.43            | -0.45              | 0.12              | 0.24               | -0.32              | -0.49              | -0.08            |
|          | -0.28           | -0.088          | 0.09             | -0.24              | -0.50             | 0.33               | -0.02              | -0.35              | 0.76             |
| Ni       | 0.004           | 0.69            | 0.04             | 0.38               | -0.05             | 0.01               | 0.12               | 0.07               | -1.4            |
|          | -0.03           | 0.40            | -0.12            | -0.20              | 0.046             | 0.56               | 0.34               | -0.48              | -0.24            |
| Zn       | 0.36            | 0.16            | -0.13            | 0.57               | 0.012             | -0.17              | 0.16               | 0.305              | -0.45            |
|          | 0.28            | 0.70            | 0.23             | -0.066             | 0.004             | -0.09              | -0.04              | 0.34               | 0.05             |
| Cd active forms | 0.01           | -0.25           | 0.03             | -0.37              | 0.55              | -0.03              | 0.65               | -0.15              | -0.6            |

We revealed plants -accumulators of some pollutants with correlation coefficients (R) for the surface layer of the soil:

- *Arctium lappa L* accumulates active forms of Pb (R²= 0.4 at P<0.01) and total forms of Ni (R²=0.69 at P<0.05);
- *Cichorium intybus L.* extracts from the soil only total forms of the following elements: Pb (R²=0.72 at P<0.05), Cu (R²=0.49 at P<0.05), Zn (R²=0.59 at P<0.05).
- *Taraxacum officinale Wigg* accumulates Cu, as well as total forms (R²=0.14 at P<0.01) and active ones of this element (R²=0.12 at P<0.01). Ground part of *Taraxacum officinale Wigg* is an accumulator of total forms (R²=0.24 at P<0.05) and active forms of Cr (R²=0.33 at P<0.05), as well as active forms of Ni (R²=0.56 at P<0.05).

*Polygonum aviculare L.* most actively absorbed from the soil the most dangerous heavy metals (Pb and Cd). The concentration of metals in the plant organs reliably correlates with the content of the total form of Pb in the soil (R²=0.57 at P<0.05) and the active form of Cd (R²=0.65 at P<0.05). In addition, the vegetative part *Polygonum aviculare L.* accumulates active forms from soil of Co (R²=0.42 at P<0.05).

Ground part of *Achillea millefolium L.* is a good remediator of active forms of Cr (R²=0.76 at P<0.05).
Another potential remediator of Cd is *Plantago media L*. and a statistical analysis of the data showed a reliable relationship between the concentration of the element in the plant and active form of the element in the soil ($R^2=0.55$ at $P<0.05$).

We have identified the plants with the highest potential for phytoremediation: *Polygonum aviculare L.*, *Plantago media L.*, *Taraxacum officinale Wigg.*, *Cichorium intybus L.*, *Chelidonium majus L.*, *Arctium lappa L.*, *Elytrigia repens (L.) Nevski*, *Artemisia vulgaris L.*, and *Achillea millefolium L.* In addition, the analysis of Table 3 showed the differences between the pollutant metals in their ability to accumulate elements (a number of metals to reduce their concentration in plants): Cr – Cu – Cd – Co – Ni – Zn – Pb. Effective remediators of available forms of Cd are *Polygonum aviculare L*, *Plantago media L.* and *Arctium lappa L.*

4. Conclusion

Thus, the analysis of the frequency and degree of exceeding the MPC of heavy metals in soils and plants indicates the presence of a directly proportional relationship between the indicators. This fact is an indirect evidence of the relationship between soil and plants. Analysis of plant samples showed differences between the biogenicity of pollutant metals and their accumulation by plants. (in raw Cr – Cu – Cd – Co – Ni – Zn – Pb).

On the basis of the obtained results, we recommend to use in the implementation of works on cleaning of soils contaminated with Pb to use *Cichorium intybus L.*, *Polygonum aviculare L.* and *Arctium lappa L.* The plants *Polygonum aviculare L.* and *Plantago media L.* show high remediation potential towards cadmium.

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