Phytomining Perspectives in Rehabilitation of Mining and Industrial Areas of South Ural

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Abstract. The ability of midland hawthorn (Crataegus laevigata (Poir)), common barberry (Berberis vulgaris), red elder (Sambucus racemosa), cinnamon rose (Rosa cinnamomea L.), couch grass (Elytrigia repens), crested wheat grass (Agropyron cristatum), meadow fescue (Festuca pratensis) and meadow grass (Poa pratensis) for phytoextraction of heavy metals from technogenic soil is proved in the article. The possibility of effective phytoextraction with the use of hawthorn and elder is shown. Maximum accumulation of zinc takes place in the surface mass of couch grass and meadow fescue. In regard to the conditions of South Ural, planting of elder and hawthorn with seeding of couch grass and meadow fescue is recommended for phytomining purposes.

1. Introduction

High concentration of manufacturing plants with extremely ineffective technological processes generates extremely tense ecological environment in Chelyabinsk oblast.

Chelyabinsk, Magnitogorsk and Karabash are in the black list of the most polluted Russian cities. According to space observations data, the main territories polluted by heavy metals are situated around Chelyabinsk and Magnitogorsk. 52% of the Oblast territory is polluted by the mill waste of iron and non-ferrous works, mining and coal industries. According to statistics data, pollutants emission into the atmosphere in a year per each citizen of Russia amounts to 372 kg of repugnant substances, in Chelyabinsk oblast this ratio varies from 200 to 2000 kg, and in Karabash it reaches 25 kg in a day. Concentration of heavy metals in soils of the mentioned territory varies in a wide range from 10 to 1500 and more mg/kg [1].

Restoration of technogenic landscapes is one of the pressing issues of modern age, especially in mining and industrial areas. The choice of treatment methods for such territories is determined by its climatic conditions, by the type, level and form of pollution, by features of the landscape and by the technologies used for obtaining the end product of a mining and processing complex.

In recent years, phytoremediation methods which provide phytoextraction (or phytomining) – metal removal by their accumulation in plant bodies – are met with wide recognition. This method is more beneficial compared to other methods of contaminated territories treatment: it is low-cost, and there is an opportunity to obtain additional products. Nowadays phytomining is defined as a usage of green plants for commercial extraction of metals of value from soil with their high concentration [2].
Aboveground parts of plants, from which the produced metals are extracted by the method of combustion, are used for phytomining.

Phytomining technology is currently under intensive development, and there are already some reports about successful testing [3-9].

Phytomining technology development is preceded by multiple research works on studying the regularities of metals accumulation in plant bodies, growing in contaminated soils. Research on developing ecological technologies (biological remediation of anthropogenic landscapes formed as a result of mining industry activities) and on their further practical use (especially in agriculture), have been conducted for almost half a century.

Phytomining is considered as a phytoextraction technology which allows extracting economically valuable metals from a substrate (in particular, from the dumps of mining industry). At that, the key role in phytoextraction and phytomining belongs to the plants – hyper-accumulators of metals. Such plants must absorb metals from the substrate, hold them in root tissues, and then transport them to the aboveground part.

The ability to form a big amount of aboveground biomass during one growing season, the simplicity of harvesting, the ability to grow and develop in unfavorable conditions are also important features of the plants – hyper accumulators of metals, primarily determined by the substrate’s specificity [10].

The considered disadvantages of heavy metals phytoextraction are: comparatively shallow substrate cleaning depth depending on the rooting depth of the used plants, and the slow rates of extracting heavy metals from the substrate. But if we consider phytoextraction as a method of obtaining heavy metals from industrial wastes, then the effectiveness and speed of phytoextraction are determined from economic point of view [11].

Different types of plants can be used as phytoextractors. Specifically, the authors have elaborated and implemented technologies for phytoaccumulation of heavy metals from waste water [12] of shrubs and grass, which are sustainable to industrial pollution and which are capable to accumulate heavy metals of high concentrations inside their tissues and organs.

In present article, the ability of local plant community representatives to accumulate heavy metals while growing on technogenic soils in the region of Karabash city is studied.

2. Objects and methods of research

Object of research in present article is the soil from territory of Karabash Mining and Metallurgical Combine. The properties of technogenic soils selected at the Karabash Mining and Metallurgical Combine, and also the amount of heavy metals contained in them, are presented in Table 1.

Midland hawthorn (Crataegus laevigata (Poir)), common barberry (Berberis vulgaris), red elder (Sambucus racemosa), cinnamon rose (Rosa cinnamomea L.), couch grass (Elytrigia repens), crested wheat grass (Agropyron cristatum), meadow fescue (Festuca pratensis) and meadow grass (Poa pratensis) had been tested as accumulators of soil metals.

Research had been conducted for three years: from 2012 till 2014. Botanic areas with single-crop sowing of sample herbs and shrub planting had been created in the field environment. Surface of each area amounted 1m². The top soil was hoed to a depth from 10 to 15 cm. Studies were conducted in three replications.

In the vegetation process, metals accumulation in the dried biomass of the plants had been assessed every 15 days. Content of metals in plant ash had been determined by the method of ISP plasma spectroscopy on the basis of standard practice.
Table 1 – Physical and chemical properties, agrochemical properties and heavy metals content in the soils, selected at the territory of Karabash Mining and Metallurgical Combine

| Parameter                                      | Soil from the Combine territory | Soil from tailing dump | Soil from the Rizhy ruchey (Red Creek) territory |
|------------------------------------------------|---------------------------------|------------------------|--------------------------------------------------|
| pH of aqueous suspension                       | 4.6                             | 2.7                    | 3.5                                              |
| pH of saline suspension                        | 4.1                             | 2.5                    | 3.2                                              |
| P$_2$O$_5$, mg/100 g                           | 10.2                            | -                      | -                                                |
| NO$_3^-$, mg/100 g                             | 1.9                             | 0.7                    | 1.1                                              |
| Dense deposit of aqueous extract (before the washing process), % | 0.34                            | 0.56                   | 1.98                                             |
| Dense deposit of aqueous extract (after the washing process), % | 0.27                            | 0.42                   | 1.31                                             |
| Organic matter (according to Turin), %         | 18.2                            | 0.87                   | 9.8                                              |

Gross content of metals

| Fe$_2$O$_3$, mg/kg                              | 15063.7                         | 49983.2                | 5157.0                                           |
| Cu, mg/kg                                       | 3075.0                          | 6687.8                 | 583.0                                            |
| Ni, mg/kg                                       | 456.3                           | 525.7                  | 30.2                                             |
| Zn, mg/kg                                       | 2639.5                          | 6112.2                 | 234.0                                            |
| Pb, mg/kg                                       | 241.3                           | 379.6                  | 215.0                                            |
| Cd, mg/kg                                       | 1.23                            | 3.5                    | 2.83                                             |

Content of mobile fractions

| Fe$_2$O$_3$, mg/kg                              | 215.2                           | 2195.5                 | 172.6                                            |
| Cu, mg/kg                                       | 35.7                            | 110.7                  | 44.8                                             |
| Ni, mg/kg                                       | 3.6                             | 10.3                   | 2.8                                              |
| Zn, mg/kg                                       | 8.1                             | 120.5                  | 2.03                                             |
| Pb, mg/kg                                       | 2.26                            | 11.2                   | 2.36                                             |
| Cd, mg/kg                                       | 1.2                             | 1.3                    | 0.95                                             |

In Table 2 common physical and water-physical properties of soils are given.

Table 2. Common physical and water-physical properties of soils

| Sample                                         | Density, g/m$^3$ | Particle density, g/m$^3$ | Total porosity, % | Capillary moisture capacity, % |
|------------------------------------------------|------------------|---------------------------|-------------------|--------------------------------|
| Soil from the Combine territory                | 1.27             | 2.05                      | 57.36             | 21.74                          |
| Soil from tailing dump                         | 1.02             | 3.15                      | 67.39             | 27.32                          |
| Soil from the catchment territory of the Red Creek | 1.19             | 2.53                      | 59.84             | 24.96                          |

3. Results and discussion

Average research results on soil metals accumulation in plants on 105 days’ exposure are given in Table 3.

As it follows from the given data, shrubs show the highest accumulation ability. Accumulation coefficient of zinc and copper in them is practically 10-20 times higher than in the reference area. Accumulation coefficient of metals in the roots is 20-45% higher than in the leaves.
## Table 3. Accumulation of heavy metals in green plants, mg/kg of dry weight

| Plant                        | Content, mg/kg of dry substance | Fe$_2$O$_3$ | Cu | Ni | Zn | Pb | Cd |
|------------------------------|---------------------------------|-------------|----|----|----|----|----|
| **Shrubs**                   |                                 |             |    |    |    |    |    |
| Midland hawthorn Crataegus laevigata (Poir) (leaves) | 52.4 | 84.2 | 10.53 | 64.23 | 2.35 | 0.13 |
| Midland hawthorn Crataegus laevigata (Poir) (roots)    | 102.36 | 100.24 | 11.25 | 112.5 | 7.36 | 3.07 |
| Common barberry Berberis vulgaris (leaves)             | 85.12 | 93.54 | 14.15 | 68.23 | 12.85 | 2.12 |
| Common barberry Berberis vulgaris (roots)              | 142.3 | 120.6 | 15.2 | 145.34 | 16.34 | 3.87 |
| Red elder Sambucus racemose (leaves)                   | 64.12 | 88.41 | 13.18 | 87.12 | 10.64 | 3.14 |
| Red elder Sambucus racemose (roots)                    | 150.3 | 126.4 | 14.36 | 135.3 | 15.43 | 6.35 |
| Cinnamon rose Rosa cinnamomea L. (leaves)              | 47.15 | 80.54 | 9.57 | 74.1 | 7.96 | 0.19 |
| Cinnamon rose Rosa cinnamomea L. (roots)               | 98.7 | 112.2 | 13.2 | 125.0 | 12.21 | 2.36 |
| **Reference areas**                                      |                                    |             |    |    |    |    |    |
| Midland hawthorn leaves/roots                           | 4.6/7.8 | 3.2/6.4 | 0.9/2.8 | 0.7/1.5 | -/- | -/- |
| Common barberry leaves/roots                            | 7.3/12.2 | 6.4/10.4 | 1.2/4.1 | 0.9/2.7 | -/- | -/- |
| Red elder leaves/roots                                  | 6.9/14.1 | 5.6/12.2 | 1.4/5.2 | 1.3/2.4 | -/- | -/- |
| Cinnamon rose leaves/roots                              | 3.3/6.4 | 3.4/9.8 | 0.8/4.5 | 1.2/1.8 | -/- | -/- |
| **Permanet grasses**                                    |                                    |             |    |    |    |    |    |
| Couch grass Elytrigia repens (aboveground part)         | 215.6 | 7.3 | 9.65 | 50.23 | 2.01 | 2.1 |
| Crested wheat grass Agropyron cristatum (aboveground part) | 179.6 | 27.3 | 8.69 | 49.6 | 1.23 | 2.78 |
| Meadow fescue Festuca pratensis (aboveground part)      | 220.2 | 26.4 | 10.2 | 56.2 | 2.03 | 3.16 |
| Meadow grass Poa pratensis (aboveground part)           | 140.12 | 20.2 | 7.2 | 50.3 | 1.36 | 1.63 |
| **Reference areas**                                      |                                    |             |    |    |    |    |    |
| Couch grass                                              | 10.3 | 2.1 | 0.9 | 2.4 | -/- | -/- |
| Crested wheat grass                                      | 8.9 | 5.8 | 0.7 | 3.8 | -/- | -/- |
| Meadow fescue                                            | 12.6 | 5.1 | 1.2 | 5.7 | -/- | -/- |
| Meadow grass                                             | 18.2 | 3.6 | 0.4 | 4.6 | -/- | -/- |

Herbaceous plants possess far lesser accumulation ability; accumulation coefficient does not exceed. Plant biomass, after planting on contaminated areas, can be used as biological ore material after burning. As it is stated in preliminary research, the combustion of plant biomass can be conducted at a temperature 300 degrees. The obtained ash can be processed with the use of pyrometallurgical method as refuse burnouts, in accordance with the reference book ETS 3-2015, Copper Industry.
The ability of midland hawthorn (Crataegus laevigata (Poir)), common barberry (Berberis vulgaris), red elder (Sambucus racemosa), cinnamon rose (Rosa cinnamomea L.), couch grass (Elytrigia repens), crested wheat grass (Agropyron cristatum), meadow fescue (Festuca pratensis) and meadow grass (Poa pratensis) for phytoextraction of heavy metals from technogenic soil had been tested. The possibility of effective phytoextraction with the use of hawthorn and elder is shown. Maximum accumulation of zinc takes place in the surface mass of couch grass and meadow fescue. In regard to the conditions of South Ural, planting of elder and hawthorn with seeding of couch grass and meadow fescue can be recommended for phytomining purposes.

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