Soil degradation and remediation

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Abstract. The global areas of degraded and diseased soils exceeded 1.2 billion hectares, that is, about 22% of the world’s agricultural lands. Losses from damaged soils account for ~25% of the global crop. In addition, land is contaminated with heavy metals and radiation, especially in mountainous areas. The aim of the work was the study and analysis of soil remediation. The issue of using grass mixtures in phytoremediation and soil remediation has not been studied enough, therefore, the problem of using new plant species that can accumulate the pollutants from aboveground biomass, is considered. In the process of studying plants on toxic soils, their accumulating abilities were determined and used as phyto-meliorants. In separate experiments, the “phyto-indicator” plants mixed with annual plant species were used, which, when the maximum biomass was accumulated, were plowed into the soil mixed with zeolite-containing clays of local importance. The experiments’ results showed that with the help of indicator plants it is possible not only to improve soil fertility, but also significantly reduce the amount of heavy metals, oil products, radionuclides, residual effects of chemical agents to control weeds, diseases and pests. Organic waste of agricultural production, waste from alcohol production, as well as the leaf litter embedded in soil with biological products were of great importance in reducing soil toxicity. The results of the experiments showed a significant reduction in toxicants in the soil when using organic waste and plowing plants as green fertilizer mixed with zeolite-containing clays and biological products.

1. Introduction
Modern urbanized territories in the regions with mining activity, represented by soil (s) as well as surface and groundwater, are subject to very noticeable pollution, both from technogenic and natural sources [1-3]. Urban areas are in constant development, which suggests their regionalization using modern approaches and equipment [4-7].

For the purpose of soil remediation, at present, natural and chemical agents are used. A special place is taken by the approach based on the plants use, both as a marker of pollution and as a powerful means of soil remediation. Under conditions of anthropogenic pollution, particular importance is attached to the question of how available plants are already resistant, for example, to heavy metals. There are several methods for checking this characteristic, in particular, a comparative measurement of the root growth rate and the comparative protoplasmic method [8-10].

The dense buildings’ impact on the soil, which usually occupies convenient and advantageous locations, depending on the pollution source occurs unevenly. For this reason, the purification (remediation) of soils from the excess pollutant masses is a very urgent and at the same time difficult task. One of the possible ways to solve this problem can be phytoremediation - cleaning the soil cover from pollution by cultivating plants that actively absorb pollutants. Phytoremediation is a highly effective technology for cleaning a number of organic substances. In this case, plants can be used to
clean solid, liquid, and air substrates [11-14]. To increase the efficiency, phytoremediation can be used in combination with other bioremediation methods and non-biological cleaning technologies. For example, the most contaminated parts of the substrate can be removed by excavation, after which further purification can be carried out using plants [15].

A number of the following plants can be used as such filters: corn, camelina, mustard, lettuce, oats, barley, peas, beans, perennial herbs, etc. Grass mixtures should be selected for the specific climatic conditions of the regions, taking into account the ability of individual crops to accumulate the polluting substances in the aboveground biomass [16-19]. Also, they should be undemanding to soil fertility (mesotrophs or oligotrophs) and capable of growing in severe pollution conditions. The main classification criterion for the proposed grass mixtures was the method of the land disturbance or pollution.

2. Research methodology

Our research was aimed at remediation of the contaminated soils by means of filter plants with sorption ability. These are the following plants: amaranth, legumes (their crop residues), legumes, ragweed, stevia, corn stalks, sunflower baskets, oilseeds. (Camelina sativa, ramtil, Crambe and others). Along with plants for soil remediation, zeolite-bearing clays of local origin (mountains and foothills of the North Caucasus), as well as biological fertilizers, providing restoration of the damaged soils, were introduced. The experiments were carried out at the experimental sites of the Gorsky State Agrarian University, the Geophysical Institute and the North Caucasus Research Institute of Mining and Piedmont Agriculture, VSC RAS, North Ossetian State University named after K.L. Khetagurov, Complex Research Institute of RAS named after Kh.I. Berbekov (Grozny).

In another experiment, to reduce the soils’ radioactivity, the seeds of legumes were enveloped with a mixture of crushed baskets of sunflower and corn stalks, Allanite clay and molasses in a ratio of 1: 10: 1. On the mowed plot at the end of the vegetation season, a layer of fallen leaves of wood crops was placed in a mixture with Allanite at a dose of 2-2.05 t / ha [16,17].

In the area contaminated with radionuclides (strontium, cesium, thorium), where radiation exceeds 1.2 micro Sv per hour, small-seeded perennial leguminous plants were sown with the advantage of creeping clover (Trifolium repens L.) - 8 kg / ha, variable alfalfa (Medicago Sativa L.) - 6 kg / ha of Galega orientalis (Galeqa orientalis Lam) - 6 kg / ha. The total mixture of legumes was 20 kg / ha. Taking the peculiarities of clover creeping to distribute root offspring throughout the territory, covering the site already in the first year of life into account, it can be assumed that the seeding rate of this type of grass was increased as a component with a larger assimilation surface for heavy metals and radionuclides’ sorption.

Before sowing, the seeds of legumes were enveloped with a mixture of crushed stalks and baskets of sunflower in equal proportions of 5 kg / ha of each component. 50 kg / ha Allanite - zeolite-containing clay and as a binder - molasses - waste starch production 5 kg / ha [18] were added to them. In heavily clogged areas, a mixture of winter camelina was sown in a mixture with clover annual Persian clover, as a culture with a high allelopathic peculiarity. No herbicides were used in these areas.

The soils of the studied areas were mainly represented by medium-power heavy loamy leached chernozem, underlain by pebbles with a large amount of coarse sand in the upper horizons (8-14%). This type of soil has, as a rule, a large water-holding ability with a sufficient content of humus and nutrients and has good physical properties. In some areas the pebbles come to the surface. The reaction of the leached chernozems soil solution ranges from slightly acidic to close to neutral (pH of the salt extract is 5.48-6.92).

To carry out the numerous studies, zeolite-containing clays with the content of macro- and microelements were widely used (Table 1).

| Chemical substance | Irlit 1 | Irlit 7 | Allanite | Leskenite | Dialkulitis | Tereklit |
|--------------------|--------|--------|----------|-----------|-------------|---------|
| Silicon (SiO₂)     | 40.2   | 52.6   | 51.7     | 50.8      | 46.4        | 56.4    |
| Aluminum (Al₂O₃)   | 16.2   | 28.1   | 16.05    | 1.1       | 18.1        | 19.4    |

Table 1. The chemical composition of local zeolite-containing clays, %
In small doses, clay (0.2-1%) contains silver, tin, molybdenum, barite, cobalt, nickel, vanadium, chromium and germanium. In terms of chemical composition, these clays also differ, which makes it possible to restrain the migration of toxic substances contained in the areas disturbed by mining operations. Silicon contained in clay (about 50%) has a high sorption capacity, absorbing toxic substances. Natural sources of raw materials contain clay particles in the range of 30-40%, coarse inclusions in the range of 2-15%. The combination of these clays in the formed ridges makes it possible to reduce the toxicity of contaminated substances and fasten them to the aggregate state by clays. In most cases, Allanite clay was used with a slightly alkaline reaction on soils with an acidic reaction of the medium. Allanite clay with a high calcium content and alkaline reaction (pH - 9.3) reduces the metal acidity.

Corn stalks - a waste of starch and syrup production (1 kg of corn contains 200 kg of rods) have high solubility, sorption ability, neutral reaction of the medium (pH - 6.9 - 7.1), no resins, wax, complete absence of heavy metals and a complex of trace elements. All of these indicators characterize corn stalks as ideal organic filters. Dissolving in the post-alcohol stillage, they enrich it with a complex of nutrients for the soil microflora development and at the same time softening, which does not require preliminary grinding.

Corn stalks contain 41.7% cellulose; 37.2% chemo-cellulose; 8% lignin; 0.08% fat; 1.75% protein; non-azotic extractives -61.7%. When grinding, the protein content in the stitches increases to 4.34-1%; non-azotic extractives -65.1% [15,16].

Calcium contained in Allanite reduces the stillage acidity, neutralizing the imposed Allanite substrate. The humid environment of the stillages and stalks reduces the amount of dust particles in contaminated areas [17, 18].

Molasses - a waste of sugar production - contains 20-25% of water, mainly amides; 58-60% carbohydrates, mainly sugar and 7-10% ash. In this object, as a binding mixture of corn stalks, baskets of sunflower, Allanite is used in amount of 5 kg / ha.

On a site contaminated with radionuclides (Sr, Cs and Th), with an area of about 1 ha, in the mining industry (Fiagdon village of North Ossetia-Alania) seeds were prepared for sowing at the rate of creeping clover - 8 kg / ha, alfalfa variable - 6 kg / ha Eastern goatskin - 6 kg / ha. Corn stalks and sunflower baskets of 5 kg / ha each were ground up. 50 kg / ha of Allanite and 5 kg / ha of molasses were added to them. All ingredients were mixed, and the seeds were enveloped in a pellet mill, after which they were sown with a conventional grain seeder. At the beginning of budding phase, the green mass per year of sowing was mowed and disposed in the specially prepared trenches for burial. At the end of the vegetation season - in autumn, the contaminated site was covered with a layer of leaf litter of wood crops collected from forest park sites in the amount of 1-2 tons per hectare, which was mixed with 2-2.5 tons of Allanite [19].

In the area contaminated with radionuclides of 0.5 hectares in spring, Coronilla motley was sown in the amount of 15 kg / ha. At the end of the vegetation season, the mass was mowed, raked, taken out and disposed of in special trenches 60-70 cm deep. Before “leaving” in the winter (late October), ground Allanite clay of local origin was applied at a dose of 4.5 t / ha to the surface of the plot, scattering evenly in the contaminated area with a layer of 4-5 cm. The next year, in the budding phase (1 mowing), the Coronilla biomass was mowed by a mowing machine and disposed. Before leaving for the winter, the mowed grass of the knit was covered with a layer of 2-3 cm Allanite at the rate of 2-3 t / ha.

| Substance     | 1.06  | 4.27  | 5.5   | 4.6   | 5.2   | 5.5   |
|---------------|-------|-------|-------|-------|-------|-------|
| Iron (FeO)    | 3.23  | 2.18  | 2.18  | 2.18  | 2.62  | 1.68  |
| Phosphorus (P2O5) | 0.4   | 0.5   | 0.38  | 0.26  | 0.28  | 0.64  |
| Calcium (CaO) | 15.3  | 3.05  | 32.6  | 28.6  | 37.0  | 2.75  |
| Magnesium (MgO)| 1.82  | 1.71  | 0.8   | 1.4   | 1.6   | 1.6   |
| Potassium (K2O) | 1.89  | 2.09  | 0.8   | 0.76  | 0.9   | 2.2   |
| Sodium (NaO)  | 0.78  | 1.1   | 0.82  | 0.64  | 0.96  | 1.4   |
| pH            | 6.9   | 3.0   | 9.3   | 8.6   | 9.1   | 7.1   |
3. Research results

An enriched area with organic substances significantly reduces toxicity and restores a fertile layer suitable for cultivating crops. At the same time, the restoration of the contaminated sites was carried out on the utilized waste basis of the stillage and corn stalk, mixing them with local natural zeolite-containing clays. By adding corn stalks to the Allanite substrate, the aeration of the area and its filtration are improved. The experiment results are summarized in Table 2.

Table 2. Heavy metal reduction

| Experience Options                      | Pb  | Zn  | Cu  | Cd  | Fe  | Pb  |
|----------------------------------------|-----|-----|-----|-----|-----|-----|
| Control (no improvement)               | 12.9| 136.0| 78.0 | 0.64 | 28.0 | 4.2 |
| Allanite coatings                      | 8.6 | 8.0 | 39.0 | 0.52 | 22.0 | 5.4 |
| Corn stalks + spirit stillage          | 5.6 | 39.0 | 21.0 | 0.34 | 16.0 | 5.9 |
| Cresting + Allanite layer              | 2.1 | 14.0 | 13.6 | 0.22 | 9.6  | 6.2 |
| Allanite clay + corn stalks + spirit stillage + sowing perennial herbs | 0.2 | 8.0 | 9.2 | 0.01 | 4.5  | 6.8 |

Consequently, natural zeolite-containing clays mixed with corn stalks grinded in the post-alcohol stillage allow to rehabilitate the soil disturbed by mining operations, reduce the amount of heavy metals and soil acidity (Ph) without any special costs, while at the same time utilizing the crop products and alcohol industry.

To quantitatively determine the ability of ragweed to accumulate heavy metals in the aerial mass, in comparison with other crops with similar sorption properties (clover, alfalfa, sainfoin), the experiments were conducted on the metallurgical plant territory near the highway and in agricultural land area. From the experiments it was found that ragweed has the maximum storage capacity to accumulate heavy metals. Given the peculiarity of vascular plants to concentrate heavy metals at the beginning of the vegetation season in a minimal amount, with a gradual increase in their content to the flowering phase, bioindication assessment of plants was carried out in different phases of development (stem, budding, flowering).

To reduce soil toxicity (from the herbicides introduction), amaranth plants were sown in the rows of corn, which during the growing season were fed with a mixture of biological products Baikal EM-1 and Baikal EM-5, after which, processing the rows, the green mass of amaranth was planted to the soil (Table 3).

Table 3. Soil remediation using amaranth mixed with Baikal – EM 1 biological product

| Experience Options                                      | Content nitrogen | Heavy content of metals |
|---------------------------------------------------------|------------------|-------------------------|
| Control (without herbicides and biological product)     |                  |                         |
| Herbicide application                                  | 172.0            | 32.0 15.8 4.2 28.0     |
| Processing crops with herbicides and replanting amaranth in row spacing | 121.0            | 36.4 22.6 6.9 39.6     |
| Processing of corn crops and the introduction of biological products | 180.0            | 26.2 13.2 3.8 25.5     |
| Sowing amaranth in row spacing + introduction of biological products + incorporation of green mass of | 198.0            | 21.6 8.2 2.8 28.2     |
|                                                          | 224              | 19.1 6.4 2.0 12.4      |
amaranth as green manure

Maximum permissible concentration (MPC) 32.0 6.8 35.0 46.0

From the above-described data it follows that in the proposed embodiment, due to the incorporation of amaranth plants (Amaranthus caudatus) into the soil with biological products, the amount of biological nitrogen increases, the content of heavy metals decreases to the maximum permissible concentrations and lower. The method allows to reduce soil toxicity and increase soil fertility. The experimental results are summarized in Table 4, in micro Sv per hour on average for 3 elements (strontium, cesium, thorium).

Table 4. Remediation of soils contaminated with radioactive elements

| Experience option | In the beginning of budding | After mowing and disposal | At the end of the 1st year vegetation | In the second year of life | radiation reduction % |
|-------------------|-----------------------------|---------------------------|-------------------------------------|--------------------------|----------------------|
| Before sowing herbs (control) | 1.82                        | 1.66                      | 1.42                                | 1.28                     | -                    |
| Sowing perennial grasses | 1.64                        | 1.48                      | 1.36                                | 1.16                     | 9.1                  |
| Sowing perennial legumes | 1.46                        | 1.32                      | 1.26                                | 1.14                     | 11.0                 |
| + seed coating | 0.92                        | 0.84                      | 0.78                                | 0.72                     | 43.8                 |
| Sowing perennial legumes + seed coating + Allanite | 0.78 | 0.64 | 0.62 | 0.58 | 54.7 |
| Green mass disposal at the beginning of budding | 0.66 | 0.58 | 0.52 | 0.48 | 62.5 |

The data analysis suggests that in one year it is possible to reduce the radiation level to the maximum permissible concentration (0.48 mk Sv per / hour), after all agricultural practices, the radiation level is reduced by 62.5%. From this it is possible to conclude that the proposed agricultural method allows to reduce the radiation level due to the utilized waste of vegetation and zeolite-containing clay - Allanite in the sowing year.

The contaminated soils remediation can also be carried out with the help of sowing plants of the Coronilla motley - bean component. The method is as follows. Coronilla motley, unlike the well-known vetch and other legumes sown on contaminated radionuclide soils, has a root shoot system and propagates both seeds and vegetatively (root shoots), covering the entire site with overgrown stems and thereby preserving the soil from evaporation with simultaneous destruction vegetation. The high foliage of plants (more than 60% of the total aboveground mass) and the many root branches allow the significant amount assimilation of radioactive substances from the soil and air. The amount of sorbed radionuclides per year is about 30%.

Mowed mass at the end of the growing season was removed from the site and disposed, after which it was covered with a layer of local zeolite-containing clay Allanite containing more than 30% calcium, as well as the trace elements, iron, magnesium, silicon, aluminum and others. The reaction of the Allanite medium (pH) is 9.3. In addition to sorption, the site is enriched with nutrients of Allanite clay and biological nitrogen of the Coronilla plants. Sown knitting plants covered with Allanite increase their winter hardiness due to clay brought to the surface after their mowing. In the next year (the 2nd year of life), the Coronilla plants grow a powerful aerial mass of up to 50 t / ha, assimilating up to 50% of the nucleotides in the soil. In the phase of maximum development (budding phase), the mass was mowed, avoiding the flowering phase, since the tribe is an insect-pollinated crop, and can use the entomofauna to transfer infected pollen with radionuclides to other areas (in particular, bees
can transfer part of the radioactive substances to honey). The mowed mass was disposed of again, and at the end of the growing season, before leaving for the winter, the plot was covered with an Allanite layer within 4-5 cm. In the first year of plant life, the content of Sr90 radionuclides is reduced due to the sorption capacity of the knit culture and covering it with a zeolite-containing clay layer from 0, 72 to the maximum permissible concentration of 0.42 mk Sv per/hour, in the second year from 0.61 till 0.38 mk Sv per/h and in the third year from 0.42 to 0.24 mk Sv per/hour. Cesium (Cs\textsuperscript{137}) shows a decrease in radiation from 0.84 to 0.72 mk Sv per/hour, in the first year, and in the second year – up to the maximum permissible concentrations (Table 5).

**Table 5. Phytoremediation of radioactive soils**

| Experience Options | Content in mk Sv per/hour |
|--------------------|---------------------------|
|                    | Strontium Sr\textsuperscript{90} | Cesium Cs\textsuperscript{137} |
|                    | 1\textsuperscript{st} year | 2\textsuperscript{nd} year | 3\textsuperscript{rd} year | 1\textsuperscript{st} year | 2\textsuperscript{nd} year | 3\textsuperscript{rd} year |
| Coronilla motley (without Allanite) | 0.72 | 0.61 | 0.42 | 0.84 | 0.78 | 0.62 |
| Coronilla motley. 1 mowing + Allanite | 0.66 | 0.56 | 0.36 | 0.72 | 0.62 | 0.50 |
| Coronilla motley. 2 mowing + Allanite (in the second year of life) | - | 0.46 | 0.32 | - | 0.59 | 0.46 |
| Coronilla motley + Allanite after 2 mowing (2nd year of life) | - | 0.38 | 0.24 | - | 0.45 | 0.32 |
| The percentage reduction from the indicator without Allanite | 8.4 | 38.0 | 42.8 | 21.0 | 42.4 | 48.4 |

**Summary**

The use of plants on toxic soils - accumulators such as amaranth, legumes and others can significantly reduce the soil toxicity and restore the fertility. The proposed approach also allows to reduce the radiation level due to the utilized waste of vegetation and zeolite-containing clay - Allanite in the sowing year.

Using vegetable waste from corn stalks, sunflower and alcohol industry mixed with zeolite-containing clays, it is possible to reduce pollution and rehabilitate infected areas, their acidity, soil fertility.

**References**

[1] Burdzieva О, Zaalishvili V, Beriev O, Kanukov A, Maisuradze M 2016 International Journal of GEOMATE 10 (1) 1693-1697
[2] Grigorikina G, Ramonova A, Kibizov D, Kozyrev E, Zaalishvili V, Magkoet V, Fukutani K 2017 Solid State Communications 257 16-19
[3] Zaalishvili V, Dhgamadze A, Gogichev R, Dzeranov B, Burdzieva O 2018 International Journal of GEOMATE 15 (51) 22-30
[4] Zaalishvili V, Melkov D, Kanukov A 2019 Akustika 32 279-283
[5] Zaalishvili V 2016 Measurement Techniques 58 (12) 1297-1303
[6] Zaalishvili V, Melkov D, Kanukov A, Dzeranov B, Shepelev V 2016 International Journal of GEOMATE 10 (1) 1670-1674
[7] Zaalishvili V, Kanukov A, Melkov D, Makiev V, Dzobelova L 2018 International Journal of GEOMATE 15 (51) 160-166
[8] Guljakov V 2010 Heavy metals in agro-landscape system Publishing house KubSAU 345.
[9] Voloshin Е 1997 Chemistry in agriculture 2 34-35
[10] Belyuchenko I 2005 Ecology of Kuban 2 470.
[11] Weltz N Patent for invention №2257597 IPC G01V9/00, G01N33/48
[12] Zaalishvili V, Bekuzarova S, Kasaeva O Patent for invention №2485477 IPC G01N33/48
[13] Sokaev K, Khusbaeva G 2014 Ecology of the natural environment of the city of Vladikavkaz and its suburbs 207.
[14] Bekuzarova S, Bome N, Bome A, Lushenko G, Tsomartova F, Pliev I Patent for invention IPC A01G7/00
[15] Zaalishvili V, Alborov I, Bekuzarova S, Sidakov A *Patent for invention* №2567900 IPC В09С1/00, В01В79/02, С05Г 3/04

[16] Khanieva I, Bekuzarova S, Khaniev M, Lazarov T, Boziev A *Patent for invention* №258027 IPCВ09С1/00

[17] Zherukov B, Khanieva I, Bekuzarova S, Khaniev M, Magomedov K *Patent for invention* №2444879 IPC А01В 79/02, А01В7/00, А01С21/00

[18] Bekuzarova S, Bzikov M, Dzhanaev H, Tsagareva E, Kudzaeva I *Patent for invention* №2229782 IPC F01В79/02, А01С21/00

[19] Bekuzarova S, Khanieva F *Patent for invention* №2574693 IPC F01В79/02, B09С1/00, G21F9/34.