The Study of Soil Protection in the System of the Cultivated Lands of Kemerovo Region

M A Yakovchenko, O B Konstantinova, A A Kosolapova
Kemerovo State Agricultural Institute
5, Markovtseva Street, Kemerovo, 650056, Russia
e-mail: mara.2002@mail.ru

Key words: heavy metals, soil protection, ingress sources, technogenesis, phytoremediation, phytostabilization, phytoextraction.

Abstract. The heavy metal content in the surface soils is characterized with their ingress for the given period of time. The sources of heavy metals in the soil are precipitation, seeds, dust, organic and mineral fertilizers, and others. The paper studies the heavy metal content in the soils of the waste dumps of the open-pit coal mines.

1. Introduction
The heavy metals (HM) represent a large group of chemical elements with atomic weight more than 50 c.u. They get into the soil in different ways: as a part of gas-dust emissions, precipitation, irrigation water polluted with industrial wastes, etc. A man can get "his share" of heavy metals not only directly when breathing the air and soil dust, but through the food produced at the polluted agricultural lands as well. The harmful effect of the heavy metals on human beings is that a number of their compounds are characterized with a high toxicity and cancerogenity.

The higher heavy metal concentrations significantly decrease the activity of the enzymes: amylase, dehydrogenase, urease, invertase, catalase, as well as the number of specific agronomically valuable groups of microorganisms. HM inhibit the processes of mineralization and synthesis of different substances in the soil, depress respiration of soil microorganisms, cause bacteriostatic effect, can act as a mutagenic factor. Under excessive HM content in the soil the activity of metabolic processes reduces, morphological transformations in reproductive organs' structure and other changes in soil biota take place. HM can significantly depress biochemical activity and cause variation in the total number of soil microorganisms [1].

The problem of the influence of the open-pit coal mines on the ecology of the nearby territories is being studied for about 50 years. It's known, for example, that the territories situated in the immediate proximity to the open-pit coal mines gradually become unsuitable for life. It happens because of great unfavourable influence of toxic substances contained in coal and its dust. The group of the toxic substances most dangerous to the environment consists of HM which are accumulated in the soil and are certain to be assimilated by the plants growing there [2].

If great amounts of HM get into the soil, its biological, chemical and physical properties change significantly, which leads to soil fertility deterioration. Besides, HM affect the plants directly, disturbing metabolism, reducing their productivity and products quality. There are a lot of studies...
devoted to the pollution influence on the soil properties. Some authors point to the reduction of biological activity of the soils, others note the increase in the number of separate groups of microorganisms, as well as the change in the enzymatic activity of the soils.

Under HM soil pollution the soil properties deteriorate: the soil structure destroys, its density increases, total soil space and water permeability decrease, water-air conditions deteriorate. HM soil pollution reduces humic acids content in the soil humus and increases fulvic acids content [3].

2. The research objective.
Consequently, the problem of soil purification from heavy metals is urgent for the territories of so-called environmentally unfriendly regions which Kemerovo region can be reckoned among. The research objective is to study the soils of the waste dumps of the open-pit coal mines concerning the content of HM labile forms.

3. The research object and methodology.
The studies were conducted on the soils of the territories nearby the open-pit coal mine of the enterprise LLC «Uchastok «Koksovyi» of Kemerovo region.

During the scientific research on the anthropogenic landscapes it’s planned to develop a combined technology of reducing HM content in the soil cover of coal producers’ waste dumps of Kemerovo region and nearby territories.

The scientists of Kemerovo State Agricultural Institute took soil samples to analyze heavy metal content and to compare the analysis results with MPC, APC. To take soil samples there were chosen 5 areas at the distance of 100 m from each other. 10 combined samples were taken with the help of the agrochemical drill from the depth of 0-10 cm.

While analyzing the special attention was given to the analysis of the content of labile forms of nickel and plumbum in the soil, that is available to the plants, by means of getting different extractions from it: water, extractions by acetated ammonium buffer solution with pH 4.8 or solutions 0.01 M and 1 n. Ca (NO₃)₂, 1 M NH₄NO₃, 1 M CaCl₂, 0.01 M KNO₃, diethylene triamine pentaacetic acid, etc.

The HM content was determined on the atomic adsorption spectrophotometer (AAS) in the laboratory of the Federal State Centre of Agrochemical service «Kemerovskiy».

4. Results and discussion.
The first stage of heavy metal transformation in the soil is their interaction with soil solution and its components.

Zinc oxide is more stable and less soluble in comparison with plumbum oxide and cadmium oxide. Its solubility in the range of pH 4 – 8 is more than 100 times lower than that of PbO, and almost 10000 times lower than that of CdO. In contrast to zinc oxide, plumbum oxide and cadmium oxide are unstable in water and are transformed into plumbum hydroxide and (or) plumbum carbonate and cadmium carbonate.

Partial pressure of CO₂ in the soil air exceeds one in the atmosphere many times and therefore more stable hydrocarbonates and zinc carbonate and plumbum carbonate prevail in the soil. After the solution of unstable oxides follow such reactions as cation exchange and specific adsorption.

The heavy metal ions are capable of being specifically adsorbed by soils, with relatively stable bonds of coordination type with some surface functional groups being formed. Specific adsorption is more selective than non-specific one and depends both on the properties of sorbing ions and the nature of surface functional groups, therefore heavy metals are actively adsorbed by the soils from the solutions.

Thus, HM getting into the soil during the technogenesis includes the following transformation stages: heavy metal oxides into hydroxides (of carbonates, hydrocarbonates); solution of heavy metal hydroxides (of carbonates, hydrocarbonates) and adsorption of the relevant cations of heavy metals by the solid phases of the soil; formation of heavy metal phosphates and their compounds with organic substances of the soil.
MPC of a substance acts as a characteristic of its danger to the environment. Polluting substance concentration in the emissions often turns out to be lower than MPC. However, while evaluating the pollution results under given conditions it’s necessary to take into consideration the following transformations with account of MPC of transient substances, because the resultant substances can have stronger toxic properties than the initial processes of accumulation and elimination of substances, as well as synergistic effect at their combined presence.

Heavy metals getting into the soil surface are accumulated in the soil and are slowly eliminated while leaching, absorption by plants, erosion and deflation. The first period of half-elimination (that is elimination of the half of the initial concentration) of heavy metals varies greatly: Zn – from 70 to 510 years; Cd – from 13 to 110 years; Cu – from 310 to 1500 years; Pb – from 740 to 5900 years.

HM absorption by the soils depends much on the reaction of the environment (pH). It was revealed that in the acid environment mainly plumbum, zinc, and copper are sorbed; in the alkaline one – cadmium and cobalt.

HM are protoplasmatic poisons the toxicity of which increases with the growth of atomic weight. Iron, for example, forms complex compounds like chelate with common metabolites, herewith disturbing normal metabolism of the organism. Such metals as cadmium, copper, iron (II) interact with cell membranes, changing their penetrability and other properties. High plumbum content in the soil depresses plant growth, causes chlorosis conditioned by abnormality of iron ingress.

Iron, as well as aluminum, belongs to the macroelements of the Earth crust, and such elements as copper, zinc, cobalt, manganese, nickel, plumbum, cadmium, belong to the microelements. Among the microelements there are both typically biogenic (Cu, Zn, Co, Mn) taking part in the most important enzymatic and metabolic processes in living organisms, and typical xenobiotics (Pb, Cd).

HM content (microelements and iron) in the zonal soils is conditioned, in the first place, by their content in the parent material and the tendency of soil formation. Besides, metal content in the soil depends on the amount of organic matter in its texture, the soil solution reactions and it’s connected with the migration in the soil crossover and biological cycle of elements.

Copper background content in the soils of Rostov region accounts for 31-38 mg/kg, and maximum values are characteristic of chernozem. Copper background content for chernozem of Siberia accounts for 14 mg/kg [4,5].

In table 1 there is given the total content of some metals in the soils and approxible permissible concentrations (APC) determined for the loam and clay soils (addition to the list of MPC and APC № 6229-91).

Average zinc content in the Earth crust accounts for 200 mg/kg. The soils not polluted with zinc contain it in the concentrations from 10 to 300 mg/kg. Loess-like loams of Western Siberia contain 71.7 mg/kg of zinc. Background concentration of zinc for the chernozem of Siberia accounts for 45 mg/kg.

Average plumbum content in the Earth crust accounts for 16 mg/kg; in the soils - 10 mg/kg. Plumbum distribution in the soil has significant variations with regard to both the types of soils and regions. Background concentration of plumbum for chernozem and chestnut soils of Rostov region accounts for 21 mg/kg and 27 mg/kg respectively, for chernozem of Siberia - 17 mg/kg.
Table 1. Total metal content in the soils (mg/kg of dry matter)

| Metal     | Average content | Possible range of variations | MPC | Metal     | Average content | APC    | Possible range of variations |
|-----------|----------------|-------------------------------|-----|-----------|-----------------|--------|-------------------------------|
| Cadmium   | 0.06           | 0.01-0.7                      | 2   | Molybdenum | 2.0             | -      | 0.2-5                         |
| Cobalt    | 8.0            | 1.0-40                        | -   | Nickel    | 40              | 80     | 10-100                        |
| Chromium  | 100            | 5-3000                        | -   | Plumbum   | 10              | 130    | 2-200                         |
| Copper    | 20             | 2-100                         | 132 | Zinc      | 50              | 220    | 10-300                        |
| Iron      | 38000          | 7000-55000                    | -   | Strontium | 300             | -      | 50-1000                       |
| Mercury   | 0.03           | 0.01-0.3                      | -   | Barium    | 500             | -      | 100-300                       |
| Manganese | 850            | 100-4000                      | 1500|           |                 |        |                               |

Average cadmium content in the Earth crust accounts for 5 mg/kg, in the soils - 0.1-0.3 mg/kg. Cadmium content in the soils depends on their type. In the gray forest soils cadmium content accounts for 0.65 mg/kg, in the sod-podzol soils - 0.7-2.31 mg/kg, in the chernozem – 0.7-1.0 mg/kg. In the chernozem of Siberia background content of the total cadmium accounts for 0.6 mg/kg.

Nickel is a rather widespread element in nature. Its average content in the lithosphere accounts for 80 mg/kg, in the soils - from 10 to 100 mg/kg. Nickel background content depends on texture and organic matter of the soils. Total nickel content in the sod-podzol soils of Moscow region accounts for 20-40 mg/kg. In the soils of Krasnodar region average nickel content accounts for 56 mg/kg. For chernozem of Siberia nickel background concentration accounts for 37 mg/kg.

HM total content in 15 stationary points of top soil horizon (0-10 cm) of the experimental areas of the waste dump of LLC «Uchastok «Koksovyi» was determined by the method of the atomic adsorption spectrometry (AAS) (table 2).

Copper content can be evaluated as low relatively to the average one for the chernozem of Siberia (14 mg/kg). Copper minimum content is 5.93 mg/kg, which accounts for about 41% of the average one, and maximum content is 13.08 mg/kg (93%). Average content is 8.96 mg/kg, which accounts for 64 % of the average one for the chernozem of Siberia. Zinc content is close to the the average one for the loess-like loams of Western Siberia, which accounts for 71.7 mg/kg, and is more than background content for the chernozem (45 mg/kg). Zinc minimum content accounted for 42.12 mg/kg, and maximum one – 69.17 mg/kg, average one - 54.81 mg/kg (under APC 220 mg/kg).

Total plumbum content is less than average for the chernozem of Siberia (17 mg/kg). Plumbum minimum content accounted for 9.05 mg/kg, maximum one – 15.57 mg/kg, average one - 12.32 mg/kg (under APC 130 mg/kg).

Total cadmium content corresponds to the background content of total cadmium in the chernozem of Siberia and in average accounts for 0.6 mg/kg. Cadmium minimum content accounted for 0.26 mg/kg, maximum – 0.93 mg/kg (under APC 2 mg/kg). Total nickel content is lower than background concentration for the chernozem of Siberia (37 mg/kg). Nickel average content accounted for 22.84 mg/kg, minimum – 14.36 mg/kg, maximum – 29.56 mg/kg (under APC 80 mg/kg).

Total cobalt content in the soils according to table 1 can vary from 1 to 40 mg/kg, with an average value 8 mg/kg. Average content of total cobalt in the soil of the waste dump accounted for 11.54 mg/kg, minimum – 8.93 mg/kg, maximum – 14.79 mg/kg.
Table 2. The content of the total and labile forms of heavy metals in the soils of the experimental areas of the waste dump of LLC «Uchastok «Koksovyi» of Kemerovo region

| point | copper | zinc | plumb | cadmium | nickel | cobalt | manganese | iron | laborel nickel | laborel plumbum |
|-------|--------|------|-------|---------|--------|--------|-----------|------|---------------|-----------------|
| MPC  | mg/kg  |      |       |         |        |        |           |      |               |                 |
| 1    | 13.08  | 51.76| 11.41 | 0.58    | 19.77  | 10.71  | 233.87    | 14032.26| 3.74          | 0.77            |
| 2    | 10.14  | 46.87| 12.64 | 0.93    | 25.54  | 13.40  | 261.78    | 18471.13| 2.16          | 1.92            |
| 3    | 9.62   | 49.32| 12.11 | 0.75    | 22.62  | 12.05  | 148.15    | 8101.85 | 4.45          | 1.79            |
| 4    | 10.40  | 48.09| 12.43 | 0.84    | 24.13  | 12.73  | 155.5     | 7770.27 | 1.67          | 1.11            |
| 5    | 9.21   | 51.43| 10.6  | 0.43    | 15.17  | 10.3   | 192.31    | 7451.92 | 3.65          | 2.41            |
| 6    | 7.41   | 64.4 | 9.05  | 0.60    | 26.8   | 11.9   | 170.07    | 14285.71| 4.39          | 1.44            |
| 7    | 10.78  | 53.28| 10.69 | 0.53    | 29.56  | 10.65  | 265.11    | 18965.52| 5.47          | 1.33            |
| 8    | 8.72   | 42.12| 14.77 | 0.58    | 28.85  | 9.23   | 263.7     | 15230.77| 2.66          | 1.77            |
| 9    | 8.22   | 60.07| 10.08 | 0.63    | 24.65  | 14.79  | 262.98    | 7172.31 | 3.03          | 2.32            |
| 10   | 5.93   | 69.17| 10.81 | 0.57    | 17.29  | 11.53  | 188.65    | 4669.17 | 3.97          | 1.74            |
| 11   | 6.46   | 66.59| 15.57 | 0.26    | 19.07  | 13.09  | 181.13    | 7849.06 | 3.08          | 1.67            |
| 12   | 8.49   | 42.74| 11.23 | 0.47    | 19.23  | 8.93   | 161.54    | 5000.01 | 2.65          | 1.68            |
| 13   | 9.26   | 62.74| 14.92 | 0.74    | 14.36  | 12.51  | 141.09    | 6821.71 | 1.22          | 1.89            |
| 14   | 7.37   | 46.85| 13.35 | 0.82    | 28.47  | 10.04  | 153.33    | 7986.11 | 3.03          | 1.68            |
| 15   | 9.39   | 66.85| 15.27 | 0.33    | 27.14  | 11.31  | 183.19    | 9046.11 | 4.28          | 2.14            |
| Averag | 8.96 | 54.81| 12.32 | 0.60    | 22.84  | 11.54  | 197.49    | 10190.26| 3.29          | 1.71            |

Total manganese content in the soils can vary from 100 to 4000 mg/kg, under average value 850 mg/kg (table 1). Manganese average content in the samples accounted for 197.49 mg/kg, minimum – 141.09 mg/kg, maximum – 265.11 mg/kg (under APC 1500 mg/kg), therefore it can be evaluated as very low.

A possible range of variations of total iron content in the soils is from 7000 to 550000 mg/kg, with an average content 38000 mg/kg. Iron average content in the samples accounted for 8056.90 mg/kg, minimum – 4669.17 mg/kg, maximum – 10965.52 mg/kg.

The evaluation of the level of soil pollution with heavy metals is connected with the availability of their separate forms to the plants. Total content of metals is a characteristic of their total amount. Labile forms of heavy metals are the most dangerous for the plants. The problems of soil pollution rating, including heavy metals, haven’t been solved to the full extent. Nowadays State Standard 17.4.1.02.–83 is valid, according to which chemical elements, including heavy metals, are divided into three classes of hazard with respect to toxic effect on the soil. Arsenium, cadmium, mercury, selenium, plumbum, zinc belong to the first class of hazard; cobalt, nickel, copper, chromium, molybdenum, antimony, boron - to the second class and barium, vanadium, wolfram, manganese, strontium – to the third class.

The chemical composition of the plants, as it’s known, reflects the soil composition. Therefore, excessive accumulation of HM by plants is conditioned, first of all, by their high concentration in the soils. During their vital activity plants contact only with available forms of HM, the amount of which, in turn, is closely connected with soil buffer capacity. However, the soil capability to combine and inactivate HM has its limits, and when the plants can’t cope with the heavy metal ingress, physiological and biochemical mechanisms of the plants themselves, which prevent heavy metal ingress, become very important.
Some interest is shown to the development of soil remediation technology known as phytoremediation which includes phytostabilisation and phytoextraction. Phytoremediation is important for remediation of agricultural lands in the regions with overlapping industrial and agricultural activity where heavy metal content in the soil is very high. Phytoremediation of polluted soils is a relatively «mild» and cheap way in comparison with revegetation.

Phytostabilisation is understood as a technology under which the plants resistant to heavy metals are grown on the polluted soils in order to reduce metal mobility and thereby further environmental pollution through leaching of these pollutants into the ground waters or preventing their distribution by wind and water soil erosion.

Phytoextraction is understood as a technology of selected plants cultivation on the polluted areas in order to extract heavy metals from the soils and accumulate them in the plants with their further processing. The plants extract plumbum from the polluted soils rather actively, and therefore the methods of plumbum phytoextraction, as well as other heavy metals, have, without any doubt, a great significance for soil detoxication.

The study of the soils of the waste dumps of LLC «Uchastok «Koksovyi» was planned to be done for 3 years. If in the revegetation areas the HM content turns out to be higher than APC, then according to table 3 it will be recommended to use plants-remediators in the areas under revegetation [6,7].

Table 3. Reliable correlation links of metal concentrations in the soil and plants (surface soils)

| The name of plants               | Pb | Cd | Zn | Ni | Cr | Co | Cu |
|----------------------------------|----|----|----|----|----|----|----|
| **Top soils**                    |    |    |    |    |    |    |    |
| Cankerwort (Taraxacum officinale)| +  | +  | +  | +  | +  | +  | +  |
| Great bur (Arctium lappa)        | +  | +  | +  | +  | +  | +  | +  |
| Couch-grass (Agropyron repens)   | +  | +  | +  | +  | +  | +  | +  |
| Green ginger (Artemisia vulgaris)| +  | +  | +  | +  | +  | +  | +  |
| Knotgrass (Polygonum aviculare)  | +  | +  | -  | +  | +  | +  | +  |
| Nosebleed (Achillea millefolium)| +  | +  | -  | -  | +  | +  | +  |
| Common wormwood (Artemisia absinthium) | + | + | + | - | + |  |
| Blue-sailors (Cichorium intybus) | -  | +  | +  | +  | +  | +  | -  |
| Fire-leaves (Plantago media)     | +  | +  | -  | -  | +  | +  | -  |
| **Deep soils**                   |    |    |    |    |    |    |    |
| Cankerwort (Taraxacum officinale)| +  | -  | +  | -  | -  | +  | +  |
| Great bur (Arctium lappa)        | +  | -  | -  | -  | -  | +  | +  |
| Couch-grass (Agropyron repens)   | -  | -  | +  | -  | -  | +  | +  |
| Green ginger (Artemisia vulgaris)| +  | -  | -  | +  | -  | +  | -  |
| Knotgrass                        | +  | -  | +  | -  | +  | +  | +  |
The name of plants | Pb | Cd | Zn | Ni | Cr | Co | Cu
---|---|---|---|---|---|---|---
(Polygonum aviculare) | Nosebleed (Achillea millefolium) | + | - | - | - | + | - | -
Common wormwood (Artemisia absinthium) | + | - | - | - | - | + | +
Blue-sailors (Cichorium intybus) | - | - | - | - | - | + | -
Fire-leaves (Plantago media) | - | - | - | - | - | + | -

5. Conclusions
The research hasn’t set the soil pollution higher than MPC and APC with respect to the total content of plumbum, cadmium, zinc and manganese in the territory under study. Most of the territory has a level of the content of the total forms of heavy metals in the soil – less than 0.5 of MPC.

The study of heavy metal content in the plant roughage showed the trace amounts, which represents a very small concentration (less than 0.1 of APC).

References
[1] Belyuchenko I S The problems of soil protection in the system of the cultivated land / Scientific journal of Kuban State Agricultural University 2014 - № 95 (01) – P 1-32
[2] Blaylock M J Enhanced accumulation of Pb in Indian mustard by soil-applied chelating agents / M J Blaylock D E Salt S Dushenkov et al // Environ Sci Technol – 1997 – V 31 - №3 – P 860-865
[3] Ibanez J J Future of soil science / J J Ibanez // The future of soil science / Ed A E Hartemink – Wageningen: IUSS 2006 – P 60-62
[4] Maximum permissible concentration (MPC) and approximable permissible concentration (APC) of chemical substances in the soil: hygienic regulations – М : The Federal Hygienic and Epidemiological Center of the Federal Service on Customers' Rights Protection and Human Well-being Surveillance 2006 – P 15
[5] Kolesnikov S I Kazeev K Sh Valkov The influence of heavy metal pollution on ecological-biological properties of typical chernozem / Siberian Ecological Journal 2000 - №3 – P 193-202
[6] Tyler G Heavy metal pollution and soil enzymation activity Plant and soil Biology of North-West Caucasus / Tyler G // Summaries of Latinarican Congress of Soil Science Chilt 1999 – P 206
[7] Khasanova G R Abramova L M The possibilities of restoration of biodiversity of steppe vegetation: permanent grasses sowing / Siberian Ecological Journal 2000 - №6 – P 473-476