

## CHAPTER 1

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### **SIGNIFICANCE OF TRACE ELEMENT COMPOSITION OF SOILS AND PROBLEMS OF THEIR REMEDIATION**

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*From a global perspective, modern civilization gives rise to a new society, a new state of the biosphere that is constantly changing depending on the new technologies and energy sources introduced. However, this society, permeated with myriads of connections with other organisms inhabiting the biosphere and dependent on cosmic rhythms and galactic disturbances, is transforming Nature into a qualitatively new state whose signs can be characterized in the short run as one of the natural evolutionary stages of the biosphere called technogenesis.*

*At the same time, the improvement of civilization associated with the transition of the biosphere to the noosphere is associated with a stage of “adaptation”. The latter consists in approaching the technologies of the society and using materials to a state of the material migration and/or the energy transformation which fits into relatively natural biogeochemical cycles and corresponds to Le Chatelier’s principle. In biogeochemistry, the significance of this principle is most completely reflected in the study of cycles for chemical elements and be one of the principal criteria for the formation of biogeochemistry of the noosphere.*

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## **1. INTRODUCTION**

The soil cover of the planet is one of the main blocks of the biosphere, along with water reservoirs having a dramatic impact on the entire global ecosystem as a whole. Soil is interconnected with the atmosphere, soil-forming rocks, the plant kingdom and microorganisms, animals and humans. It is the key link for biogeochemical cycles of chemical elements.

Following V.V. Dokuchaev (1994), V.I. Vernadsky showed that in none of natural bodies but soil the interpenetration between mineral substances and living organisms is so close. At the beginning of the 20th century, V.I. Vernadsky (1913) came to the conclusion that the Earth's soil cover plays a global geochemical role. This idea can be traced throughout the scientific activity of the great researcher. It is the soil that becomes one of the principal subjects of the biosphere functioning. Therefore, later on soil scientists identified soil biogeochemistry as a special research discipline (Kovda, 1979).

Despite the complexity of the task and its apparent uncertainty, these works were nonetheless carried out, one of them being a summary report by A.P. Vinogradov "Geochemistry of rare and trace chemical elements in soils" published in 1957.

Some data on trace element composition of soils, hygienic standards, biogeochemical criteria for evaluation of ecological state and phytoremediation processes are systematized. Particular attention is focused on the clarkes (average levels) of chemical elements, their deficiency state and some problems of soil.

The most common types of environmental violations are land contamination with chemical and/or radioactive substances, industrial waste and/or sewage, as well as littering. Scientific publications indicate that the intensity and the scale of soil pollution in cities and their suburbs are still more significant.

## **2. CHEMICAL COMPOSITION OF SOILS**

Chemical elemental composition is one of the characteristic features of soil. Therefore, many scientists have endeavored to integrate the scattered data on the chemical composition of soils and give average levels of the chemical elements on a global scale (i.e., clarkes).

Along with a specification of the existing factual material regarding the levels of chemical elements in the main types of the massive materials existing in the Earth's lithosphere, gives some data on their concentrations in soils. These data represented the generalized analyzes of some 20 key soil sections made in the European part of the former USSR as well as other numerous literature data.

Table 1 summarizes the data on the average chemical element levels in soils worldwide (clarkes) including those obtained by A.P. Vinogradov (1957), H.J.M. Bowen (1979), H.T. Shacklette and J.G. Boerngen (1984), and V.A. & A.V. Alekseyenko (2013). Separate columns represent the calculated variation ranges of the mean values (VR), also some supplementary data from the authors or other researchers are given.

The list made by A.P. Vinogradov (1957) is not the comprehensive one, the largest amount of the data being presented by G. Bowen (1979). The lists compiled by the other authors practically duplicate the one by A.P. Vinogradov (1957).

The VR averages from various scientists are given for 28 trace elements. Of these, the VRs up to 2 units are characteristic for 13 chemical elements, the ones > 2 to 5 units for 9 chemical elements and those > 5 for 6 microelements. Also, there are chemical elements showing very high RVs. The latter ones include beryllium (20 units), selenium (40 units), silver (10 units), tin (7.69 units) and mercury (9 units). It is noteworthy that the data summarized in Table 1 represent average indices for soils worldwide. They differ from the median values. Thus, according to G. Bowen (1979), the average levels for Cr, Co, Ni, Zn, As, Rb, Sr, Y, Zr Nb, Ce are 70, 8, 50, 90, 6, 35, 250, 30, 400, 10, 50 and 12 mg/kg, respectively, while their median values are 80, 10, 20, 70, 5, 65, 240, 20, 230, 12, 65 and 17 mg/kg. For some trace elements, comparative analytical data exist that are available in relevant reviews (Kabata-Pendias, Pendias, 1979; Kovda, 1979; Jovanovic, 2007). For example, the background levels for antimony in the upper layers of CIS soils are as

follows (mg/kg): sod-podzolic soils 0.76, chernozems 0.99 and peat 0.28. For horizon A of soils in Canada, Great Britain, Nigeria, and Bulgaria, the average levels vary from 0.19 to 1.77 mg/kg (Tshan et al, 2009).

*Table 1. The average content of chemical elements in soils according to various authors, in mg/kg*

No	Chemical element	Vinogradov, 1957	Bowen, 1979	Shacklette, Boerengen, 1984	Alexeenko, Alexeenko, 2013	Max/Min	Ermakov, 2015
3	Li	30	25	24	30	1.25	-
4	Be	6	0.3	0.92	6	20.00	-
5	B	10	20	33	10	3.30	-
9	F	200	200	430	-	2.15	-
23	V	100	90	80	100	1.25	-
24	Cr	200	70	54	200	3.70	-
25	Mn	850	1000	550	850	1.82	-
27	Co	8	8	9.1	8	1.14	-
28	Ni	40	50	19	40	2.63	-
29	Cu	20	30	25	20	1.50	20-30 <sup>1)</sup>
30	Zn	50	90	60	50	1.80	-
31	Ga	30	20	17	30	1.76	-
32	Ge	n x 1	1	1.2	5	5.00	-
33	As	5	6	7.2	5	1.44	-
34	Se	0.01	0.4	0.39	-	40.00	0.3
35	Br	5	10	0.85	-	11.76	-
37	Rb	100	35	67	100	2.86	-
38	Sr	300	250	240	300	1.25	-
42	Mo	2	1.2	0.97	2	2.06	-
47	Ag	n x 0.1	0.05	0.05	0.5	10.00	-
48	Cd	0.5	0.35	-	0.5	1.43	-
49	In	-	1	-	1.0	-	-
50	Sn	10	4	1.3	10	7.69	-
51	Sb	-	1.0	0.66	-	1.52	-
52	Te	-	-	-	-	-	-
53	I	5	5	1.2	-	4.17	-
56	Ba	500	500	580	500	1.16	-
74	W	-	1,5	-	-	-	0.3-1.0
75	Re	-	-	-	-	-	0.0003-0.003
79	Au	-	0.001	-	-	-	0.0005-0.005
80	Hg	0.01	0.06	0.09	0.01	9.00	0.03-0.07
81	Tl	-	0.2	-	-	-	-
82	Pb	10	12	19	10	1.90	-
83	Bi	-	0.2	-	-	-	-
92	U	1	2.0	2.7	-	2.70	-

Notes: (-) - no data available; <sup>1)</sup> according to the authors

For selenium, gold, mercury, tungsten and rhenium, the background values that we have obtained for the North Caucasus and Eastern Transbaikalia are given. At present, interest in REEs has increased.

The evidence available on their background levels present in soils is scarce. The research results obtained by E.V. Dabakh touch upon horizon A of the soils of morainic landscapes present in the northeast of the European part of Russia. According to the author's data, the REE total concentrations are not high and range from 50 to 100 mg/kg (Dabakh, 2017).

D.V. Ladonin's report presents data on lanthanide levels as seen in the soils of the South-East Administrative District (SEAD) of Moscow. Their total content does not exceed 40 mg/kg. D.V. Ladonin (2016) systematized the data obtained by various researchers on the concentrations of the platinum group elements as observed in the Earth's crust and urban soils.

The article by Caritat P. and Reimann C. (2012) provides a critical review of this issue. When comparing the data given by some 8 authors on the median levels of 10 macro- and 16 microelements, the VRs varied from 1.44 to 6.80 units. At the same time, the variation of up to 2 units was typical for 11 chemical elements, the one from > 2 to 5 units for 13, and this one exceeding 5 units for 2 chemical elements (namely, Ca and Na) of the continental crust, which does not provide reliable estimates of the natural contents of the chemical elements in soil.

When analyzing quantitative parameters for 16 microelements, the authors noted that there were significant differences between the published average concentrations in soils as seen worldwide and the ones observed on two continents (Europe and Australia) although the total sampling areas were 5.6 and 6.2 million km<sup>2</sup>, respectively.

Furthermore, a direct comparison with the other continental data available was hampered as the mean values were not determined in the research works where median indices were indicated instead that were regarded as a more reliable parameter. The authors are also critical of the lithological unit global database for it seems inadequate and is a poor soil chemistry predictor.

In addition, climate-related processes such as glaciation and weathering are strong modifiers of the geochemical composition inherited from bedrock during soil formation. To overcome the existing drawbacks of

using the predicted global or worldwide soil geochemical reference values, the authors propose preliminary empirical global soil reference values based on the results of analyses of a representative number of soil samples collected in these two continents (PEGS2).

Comparison of the data is summarized in Table 2.

*Table 2. Median values of the soil chemical composition according to the data of the continental geochemical services of Europe (GEMAS Ap) and Australia (NGSA Tc), and preliminary data on the global estimation of the soil composition based on the data for the two continents (PEGS2)*

Trace element	<u>Arable land</u>	<u>Precipitation</u>	Reference value (PEGS2)
As	7	3	5
Ba	391	315	353
Ce	59	42	51
Co	9	8	9
Cr	64	48	56
Ga	12	10	11
Nb	13	9	11
Ni	21	15	18
Pb	21	13	17
Rb	75	51	63
Sr	102	68	85
Th	9	8	8
V	70	55	63
Y	28	21	25
Zn	62	31	47
Zr	263	304	284

*Source: De Caritat, Reimann, 2012*

## 2.1 On the chemical element standards for soils

Currently, in the course of biogeochemical investigations aimed at estimation of chemical element(s) environmental status, not only the “clarkes” but also some background geochemical levels and hygienic standards are used including maximum permissible concentrations (MPC) and approximate permissible concentrations (APC).

In view of aggravation of man-caused problems, researchers have begun more often applying for the standards for the permissible levels of chemical elements in soils. As a result, some discrepancies were determined between the real risk levels and the current few MPCs for chemical elements in soils (Motuzova, Karpova, 2013; Syso, 2016).

The problems of standardization have been repeatedly discussed at the International biogeochemical Schools. Thus, Professor E.V. Evstafieva (Simferopol) (2013) noted that, in accordance with the methodological recommendations of the Convention on Long-Range Transboundary Air Pollution (LRTAP) as an environmental standard for permissible levels of exposure to pollutants, various types of ecosystems use critical loads that allow taking into account their natural diversity and sustainability to man-caused impact.

Some Russian hygienic standards for environmental assessment of soils were criticized by Professor A.I. Syso (Novosibirsk) (Syso, 2016). He emphasized the poor scientific validity of the domestic APCs for inorganic soil pollutants due to the discrepancy among the determination methods, and expressed his concern that using these standards results in errors in determining the degree of soil pollution, therefore, they require further improvement.

The data quoted in the documents (Hygienic Standards, 1991, 2009) indicate that the regulatory framework used in the soil science and soil hygiene is incomplete. Hence, the development of regional standards for various types of soil taking into account soil-geochemical associations and their resistance to chemical pollution appears more justified here.

The shortage and low informative value of the existing standard parameters for chemical elements in soils (MPCs) has prompted soil scientists to develop standards using alternative approaches. First of all, a statistical technique to determine the chemical permissible levels in soils should be mentioned that involves determining the average (i.e., most common) levels of chemical elements in natural environments suggesting natural conditions.

The theoretical basis of this approach is as follows: the average content levels of chemical elements in natural environments as observed in natural conditions corresponds to the conditions of a normal state of living organisms (Motuzova, Karpova, 2013).

On this basis, critical levels for various chemical elements present in the soils in various countries were calculated (Table 3). They come close only to the standards as determined by Bulgarian researchers (Atanassov, 2008). Maximum values are characteristic of MPCs for metals as

determined in the USA. They practically characterize man-made metal deposits.

Table 3. MPC values for chemical elements in soils (mg/kg) according to the data obtained by researchers in various countries

Trace element	Reference				
	El-Bassam, Tietjen, 1977	Linzon, 1978	Kabata-Pendias, Pendias, 1979	Kloke, 1979	Kitagishi, Yamane, 1981
As	50	25	30	20	15
B	100	100	25	-	-
Be	10	10	10	-	-
Cd	5	8	5	3	-
Co	50	25	40	50	50
Cr	100	75	100	100	-
Cu	100	100	100	100	125
F	500	-	1000	200	-
Hg	5	0.3	5	2	-
Mo	10	2	10	5	-
Ni	100	100	100	100	100
Pb	100	200	100	100	-
Se	10	5	10	10	-
V	50	60	100	50	-
Zn	100	400	300	300	250

Notes: (-) no data available.

Table 4 shows comparative data on the standards of tolerance levels of metals in soils. Russian standards with their rather low values differ from the recommendations as adopted in other countries.

Table 4. Comparative tolerance levels of heavy metals in soils

Metal	Tolerant levels of metals, mg/kg					
	RF	USA	Bulgaria	Finland	Netherlands	Germany
Cd	0,5-2,0	30-800	0,6	10-20	0,8-20	10-60
Pb	32-130	300-6000	45	200-750	85-600	200-2000
Zn	55-120	2500-100000	160	250-400	140-3000	-
Cu	33-132	-	60	150-200	36-500	-

Notes: (-) - no recommendations.

Sources: (Ermakov et al., 2018a; Motuzova, Karpova, 2013; Kobes, 1998)



In some cases, in the absence of standards, soil contamination is identified as a fivefold excess of a chemical element background level as found in soil (Ilyin, Syso, 2001). Also, a method for determining heavy metal APCs in contaminated soils proposed by Yu. N. Vodyanitsky is of interest (2012).

## 2.2 On trace element deficiency in soils

It should also be noted that there are no standards yet for required microelements associated with their deficiency in soils. Nevertheless, the deficiency of some essential trace elements in plants is a common issue existing both in medicine and agriculture (Ermakov, 2015; Schulin et al., 2010) (Table 5).

Table 5. The relationship of trace element deficiency with the main types of soils

Soil group	Limiting properties	Deficiency	Additional features Problems
<b>Akrisoli</b>	Leached, with strong acidity	Most trace elements	Toxicity of Fe and Mn
<b>Andosoli</b>	Amorphous hydrated oxides	B, Mo	Toxicity of Al
<b>Arenosoli</b>	Sandy texture	Cu, Fe, Mn, Zn	-
<b>Chernozems</b>	High pH CaCO <sub>3</sub>	Fe, Mn, Zn	-
<b>Ferralsoli</b>	Highly weathered, Al and Fe oxides are accumulated	Mo	Toxicity of Al, Fe and Mn
<b>Gleisoli</b>	Waterlogging	Mn	Toxicity of Fe and Mo
<b>Histosols</b>	Accumulation of organic matter, waterlogging	Cu	-
<b>Chestnut trees</b>	High pH, CaCO <sub>3</sub>	Cu, Mn, Zn	-
<b>Planosoli</b>	Highly leached, waterlogging	Most trace elements	-
<b>Podzols</b>	Acidic, leaching, strong organ complexes	Co, Cu and most others	-
<b>Rendzins</b>	High pH, Na accumulation	Fe, Mn, Zn	-
<b>Leptosoli</b>	High pH, Na accumulation	Cu, Fe, Mn, Zn	-
<b>Solontsy</b>	High pH, Na accumulation	Cu, Fe, Mn, Zn	-
<b>Ermosoli</b>	Arid, High pH, Ca Carbonate	Co, Fe, Zn	-

Notes: (-) no data available

Source: Schulin et al., 2010

In recent years, the problems of trace element deficiencies have become even more urgent due to the following causes:

- growth of trace element demand caused by intensification of crop production;

- using low-fertility soil;
- high population growth rate and urbanization of fertile lands;
- using high-quality macronutrients with lower trace element levels;
- decrease in the bioavailability of trace elements through improper agronomical practices, e.g. at excessive liming (Ermakov, 2015).

The particular attention here is paid to the deficiency of selenium as a vital trace element. In most cases, selenium concentration in soils is 300 µg/kg. Selenium deficiency is typical for sandy soils or the ones formed on acidic igneous rocks. In addition, selenium mobility is reduced in some meadow-boggy and/or peaty soils, despite its higher concentrations (up to 1000 µg/kg). It should also be borne in mind that selenium accumulation by plants is increased on calcareous soils while the excess of phosphorus and/or iron generally inhibits the element entry into plants (Ermakov, Jovanovic, 2010).

Trace element deficiencies are becoming increasingly important both in livestock and crop production as unplowed grounds are used for grazing or forage production, which, in turn, is due to higher demand for food and requirement for other land uses. However, an ultimate solution to this problem is still ahead.

### **3. THE PROBLEM OF POLLUTION AND SOIL REMEDIATION**

By the beginning of the 90s, about 70% of the total volume of toxic industrial waste in the USSR was disposed in Russia, including all types of bulk waste like molding sand used, shale processing waste, oil sludge, galvanic sludge, oil waste, etc. Thus, more than 1.6 billion tons of toxic industrial waste has accumulated in Russia, with this figure increasing by some 50 million tons annually while just 20% of the bulk is used. Currently, about 80 thousand types of chemical products with a total volume of about 300 million tons are produced annually worldwide (State report, 2017).

Today the area of inhabited localities in Russia covers as many as 20.9 million hectares and some 17.6 million hectares more are occupied with enterprises of industry, transport, energy, etc. Thus, in Moscow region, the most densely populated region of Russia, the lands of inhabited localities comprise 10.5% while the industry, transport and

communications land - 6.4%. About 10% of urban settlements in this country exhibit higher environmental pollution levels including those for soil. The most acute environmental problems of urban land use are considered pollution, littering and disturbance of lands, as well as inadequate extent of their remediation. Also, a constant increase in the area of land subject to pollution through industrial emissions is registered (Yanin, 2014) (Table 6).

Table 6. Expert assessment of the acuteness of land use environmental problems in Russia associated with violations of land & environmental legislation or caused by land pollution)

Problems	Distribution of areas according to the severity of manifestation of environmental problems of land use					
	1		2		3	
	number of regions	% of the total area	number of regions	% of the total area	number of regions	% of the total area
Associated with violation of land and natural laws (total land area = 100%)						
Land pollution as a result of economic activities and emergencies	28.0	41.3	30.0	33.1	15.0	17.8
Disturbance of lands and their remediation	51.0	74.4	16	22.4	6.0	3.2
Soil degradation as a result of failure to comply with soil protection and other environmental protection measures	22.0	49.6	42.0	44.1	9.0	6.3
Failure to comply with federal and/or regional programs to improve soil fertility	15.0	41.1	37.0	20.5	21.0	38.4
Problems related to land pollution with as follows (total land area = 100%):						
oil and oil products	55.0	68.6	11	12.2	6.0	6.3
heavy metals	55.0	73.6	11	11.1	4.0	7.4
Agrochemicals	55.0	79.3	14	11.8	3.0	1.1
household waste	51.0	71.0	19	20.9	1.0	0.3
industrial waste	46.0	59.5	20	24.3	7.0	8.4
livestock waste	58.0	80.1	10	11.2	3.0	0.8

Note. Acuteness of the problem: 1 - manifests itself in insignificant areas and is not of high priority for the region; 2 - manifests itself and is considered as a priority in a significant area of the region; 3 - takes form of an “environmental crisis” in a part of the region.

Source: Yanin, 2014

At the same time, urban grounds are justifiably regarded as an integral and, we must add, an important part of Russia's national wealth. All these points determine the relevance of the development of both inventory survey & evaluation procedures and cleaning technologies for contaminated urban soils (Yanin, 2014 Radosavljević et al., 2018).

Military actions significantly impact the dynamics of environmental pollution. As a result of World War II, thousands of tons of metals were left on the battlefields. A relatively small-scale NATO military operation in Yugoslavia in 1999 brought about the increase in consumption of some toxic elements like lead (Pb), cadmium (Cd), arsenic (As) and mercury (Hg) as a result of air, water and soil pollution in Serbia, as well as because of inadequate quality of food products being imported or sent for humanitarian purpose (Djujic et al., 2001).

According to the State Committee for Ecology of the Russian Federation, the total effect of the military forces' impact on the environment in peacetime is comparable to the impact of one of the medium-sized industries (making some 4% of the total wastewater discharge and 1.2% of atmospheric emissions). According to the Directorate of Ecology & Special Means of Protection of RF Ministry of Defence, real emissions and discharges from military facilities/garrisons are commensurate with small or even medium-sized enterprises (Nikitin et al., 1997).

Among the man-caused changes as occurred in the habitat of organisms, the greatest concern is caused by its pollution with industrial and household waste. As noted above, toxic substances of different nature represent the greatest danger here. In our opinion, a pollutant is a man-caused or natural substance or a mixture of substances that disrupts the cycles of chemical element(s) migration and/or energy transformation, and has an adverse effect on the functioning of ecosystems in general. Pollution is a process of man-caused or natural substances entering and/or incorporating into ecosystems in amounts toxic to the ecosystems or contributing to formation of new hazardous compounds.

They can be classified according to their chemical structure, entry sources, type of production, mechanism of their effect on organisms, or their migration and transformation characteristics (Ermakov, 2005; Ermakov, Jovanovic, 2010a).

According to V.A. Korolev (2001), 3 main methodological approaches can be applied to control pollution, the first one being a straightforward soil cleanup, which calls for a direct removal of harmful components by their removal off the piece of ground, and its cleaning in one way or another. In this case, the removed pollutants are subject to further disposal outside the piece in some way.

The second approach is not based on removal, but on detoxification of the harmful component on the spot, directly in the piece of ground, for example, through its neutralizing, decomposition/destruction, binding, etc. The third approach is based on the pollutant containment right on the ground through erecting a protective shield around the anomaly that would prevent the further spread of pollution (e.g., the Chernobyl sarcophagus) (Laverov et al., 1994).

Also, some ecosystem natural self-cleaning schemes are used based on abiotic or biotic conversion of chemical pollutants. If the pollution covers the solid phase of the rock/soil or is sorbed with it, the following in situ schemes can be applied: 1) chemical neutralization + leaching or dissolution + removal of the products with solution; 2) treatment with desorbents (i.e., physicochemical methods) + biodegradation + removal of products with solution; 3) chemical or physical (thermal) curing on the spot + biodegradation + putting up a protective shield; 4) thermal destruction + leaching + removal of products with solution, localization of the contaminated area and the soil excavation (Korolev, 2001; Yeung, Datla, 1995).

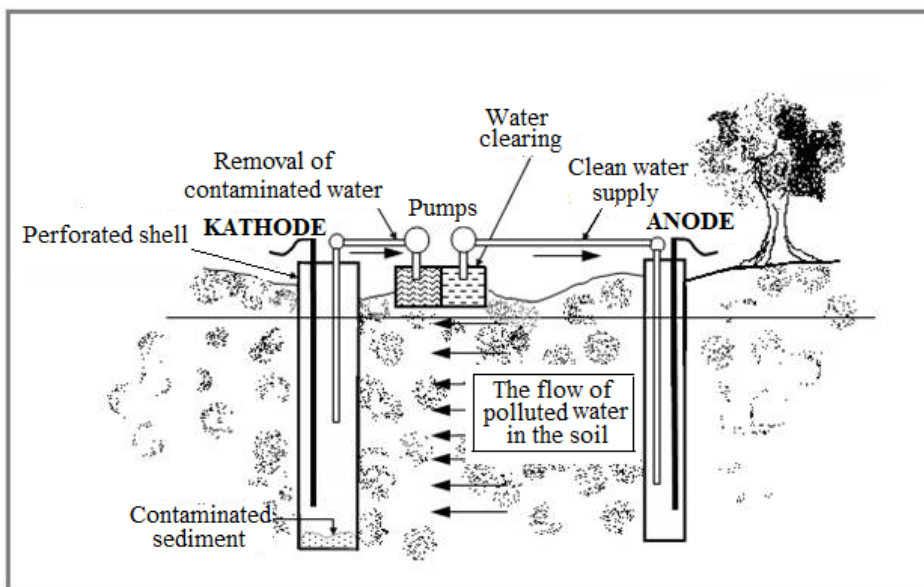
If the pollutant is present in the liquid phase of the rock mass, the following complexation schemes can be used: 1) pumping out (possibly with dilution) + water purification on the surface; 2) electrical treatment + pumping out + water purification on the surface; 3) chemical or physicochemical neutralization (precipitation) + biodegradation + protective shield (or removal of products with a solution); 4) thermal destruction + biodegradation + protective shield (or removal of products with a solution).

If the pollutant is in the gas phase or represents fixed gases, then the following schemes can be applied *in situ*: 1) heat treatment + vacuum extraction + protective shield; 2) biodegradation + vacuum pumping + washing; 3) chemical or physicochemical neutralization + washing (or vacuum pumping). The above listed cleaning methods should be also

supplemented with electrokinetics (Korolev, 2001) widely used for soil cleaning, phytostabilization and phytoextraction. For soils, methods to correct heavy metal intake due to application of appropriate fertilizers or additives are used (Galiulin, Galiulina, 2008; Morozova et al., 2015; Bashkin et al., 2019).

The physical methods for soil cleanup include electrochemical and electrokinetic techniques.

Electrochemical purification is used to remove chlorine-containing hydrocarbons, various oil products and/or phenols from soil. The electrochemical purification technique is based upon the following. While moving through the soil, the electric current accounts for water electrolysis, electrocoagulation, electrochemical oxidation and electroflotation reactions (Fig. 1).



*Fig. 1. Scheme of a field device for in situ soil cleanup using electroosmotic method. The arrows indicate the direction of the electroosmotic flow (namely, to the cathode), since the clay or silt particles (i.e., dusty soil particles) have a negative charge and therefore the DPS mantle is positive (Korolev, 2001).*

The oxidation degree for phenol ranges from 70 to 90 percent. The quality level of soil disinfection at electrochemical purification approaches 100% (the minimum value is 95%). The method also allows removing some harmful elements like mercury, lead, arsenic, cadmium, cyanides, etc. from soil. One of the disadvantages of this method is its rather high cost (\$100 to 250 per 1 m<sup>3</sup> of soil).

Electrokinetic purification is used to clean soil from cyanides, oil and/or oil derivatives, heavy metals, cyanides or organic chlorides. The soils for which electrokinetic purification can be successfully applied include the clay and the loamy ones partially or completely saturated with moisture (Korolev, 2009; Korolev, Nesterov, 2019).

The technique is based on the use of processes like electrophoresis and electroosmosis. The levels of the procedure control and its impact on soil purification are sufficiently high. This method requires the use of surfactant chemical reagents or solutions (. Yeung, Datla, 1995). The efficiency of electrokinetic soil purification ranges within 80 to 99 percent, its cost being slightly lower than that one for electrochemical purification (namely, \$100 to 170 per 1 m<sup>3</sup> of soil).

### **3.1 Chemical methods of soil cleanup include a leaching method**

The chemical soil cleaning techniques imply using surfactant solutions or strong oxidants like active oxygen or chlorine, and alkaline solutions. Basically, this method is used to clean up soil from oil. The efficiency of the leaching method is up to 99% (Korolev, 2001). After the soil is cleaned, it can be remediated. The disadvantages of the chemical methods of soil purification include long terms required (1 to 4 years on average) and significant amount of water to be contaminated that would also require purification before being released into the environment.

### **3.2 Biological methods of soil cleanup**

These include phytoextraction and phytoremediation techniques. It should be noted that the problems of phytoremediation of soils and phytoextraction of toxic substances are being widely discussed worldwide. A number of detailed reviews and monographs have addressed this issue (21, 35, 49, 64]. (Salt et al., 1998; Golubev, 2011; Koptsik, 2014; Yanin, 2014).

Phytoextraction is a technique for cleaning up harmful substance-contaminated soils through the pollutant accumulation with plants, which is associated with the cultivation of certain plant species in areas where the ground or the soil is contaminated.

Phytoextraction shows good results when cleaning soil from copper, zinc or nickel compounds, as well as from cobalt, lead, manganese, zinc or chromium. To remove the most part of these elements from soil, several cycles of plant crops are required. At the end of the phytoextraction process, the plants are collected and subjected to further processing (combustion, use as a biofuel, etc.).

About 40 plants are known to be metal hyperaccumulators. Many of them belong to the family *Brassicaceae*, primarily the genera *Alyssum* and *Noccaea* (Verbruggen et al., 2009). In particular, the Alpine pennycress is a Zn & Cd hyperaccumulator. Also, a Zn, Cu & Ni hyperaccumulator and a Ni hyperaccumulator were identified (*Arabis sagittata* and *Alyssum murale*, respectively) (Alekseeva-Popova et al., 2015; Ufimtseva, 2015; Narasimha, Prasad, 2005).

The discovery of hyperaccumulating plants capable of absorbing HMs in quantities 50 to 500 times as higher than ordinary plants triggered revolutionary development of phytoextraction techniques. Thus, a quarter of a century after the first review, about 400 hyperaccumulating plants were known, which comprised less than 0.2% of all angiosperm species that mainly belonged to the families of composites (*Asteraceae*), crucials (*Brassicaceae*), pink family (*Caryophyllaceae*), sedge family (*Cyperaceae*), cunonium family (*Cunoniaceae*), legumes (*Fabaceae*), Indian-plum family (*Flacourtiaceae*), labiates (*Lamiaceae*), bluegrass (*Poaceae*), violet family (*Violaceae*) and spurge family (*Euphorbiaceae*). Higher plants are considered to be hyperaccumulators capable of accumulating > 1 mg of Au or Ag, > 100 mg of Cd, Se or Ta, > 1000 mg of Cu, Co, Cr, Ni, Pb, U or As, and > 10000 mg of Mn or Zn per 1 kg of scions dry weight when grown on HM- and/or metalloids-enriched soils (Nikitin et al., 1997).

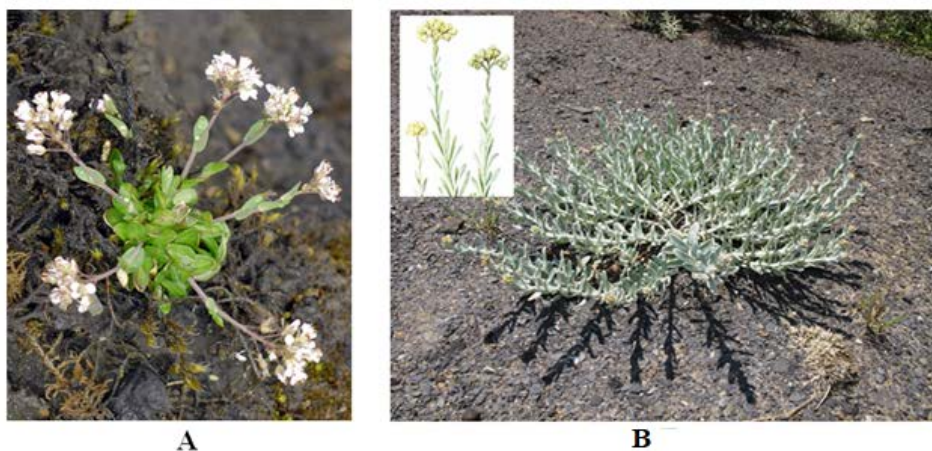
The biological absorption coefficient exceeds 1 (Alekseeva-Popova et al., 2015; Ufimtseva, 2015). There are as many as 4 hyperaccumulating species for As, 1 for Cd, 30 for Co, 34 for Cu, 14 for Pb, > 320 for Ni, 20 for Se, 11 for Zn and 10 for Mn. The ability to hyperaccumulate metals is most characteristic of representatives of the family of crucials including 11 genera and 87 species, in particular, for Ni 7 genera and 72 species, and for Zn 3 genera and 20 species. The best Ni hyperaccumulator is a small tree *Sebertia acuminata* from New Caledonia, with its dried bluish green latex containing ~ 25% of metal. Various species of pennycress



(*Thlaspi*) are capable of accumulating several metals, e.g., *T. caerulescens* plants accumulate Cd, Ni, Pb and Zn, *T. goesingense* and *T. ochroleucum* - Ni and Zn, and *T. rotundifolium* - Ni, Pb and Zn (Salt et al., 1998; Narasimha, Prasad, 2005).

Apparently, the metal hyperaccumulation phenomenon is an evolutionary adaptation of plants to survive in unfavorable habitats with high HMs levels in soils on ultrabasic rocks. The issue of what advantages the metal hyperaccumulation capacity gives to the plants remains unclear. These advantages probably include HMs tolerance, drought tolerance, an ability to compete with less tolerant plants, accidental HMs absorption or protection from herbivores or some pathogens.

The above list should be supplemented with a number of poplar and willow species that act as cadmium and/or zinc accumulators (Baltrėnas, Ćepanko, 2009; Boriřev et al., 2009; De Maria et al., 2011; Ermakov et al., 2015a; Markovskaya et al., 2015). In the area of the Unal tailings pond we discovered a new endemic metal accumulating plant species, *Cladochaeta candidissima* (*M. Bieb.*) belonging to the family of the composites and found in the Ardon river shingle deposits (Fig. 2.).

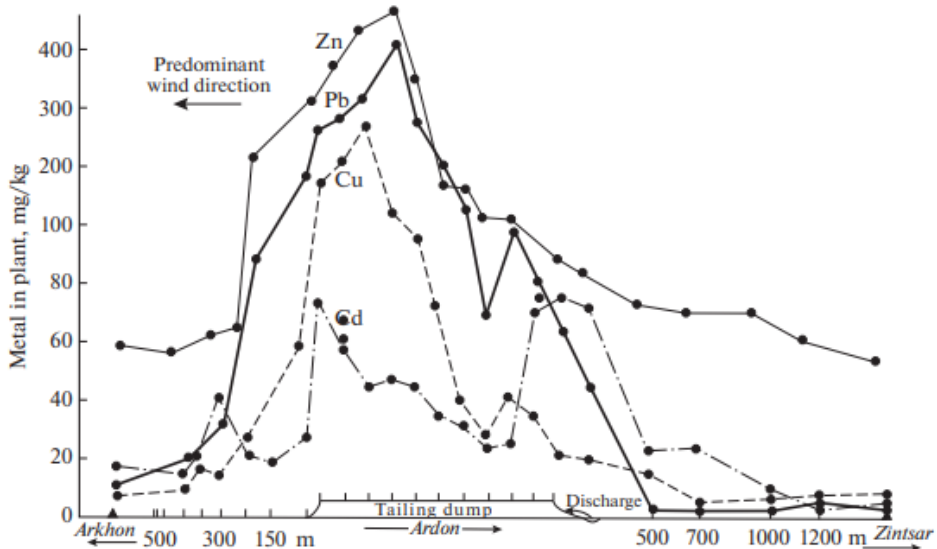


**Fig. 2.** Metal hyperaccumulating plants: A: *Noccaea caerulescens* (the Alpine pennycress) is a Zn and Cd concentrator, B: endemic of North Ossetia, the pure cladochaeta *Cladochaeta candidissima* (*M. Bieb.*)  
Source:(Ermakov et al., 2018).

Figure 3 shows the highest Zn, Cu, Pb and/or Cd levels in the samples of a plant growing in the immediate vicinity of the tailings pond. The concentrations reach 456 mg/kg (Zn), 422 mg/kg (Pb), 250 mg/kg (Cu) and 65 mg/kg (Cd) (Ermakov et al., 2018).

Phytoremediation is a targeted enhancement of the activity of the specific soil microflora which is involved in crude oil decomposition. Also, adding some microbial cultures to soil and using transgenic microorganisms that enhance organic toxicants decomposition are acceptable (Cherian, Olivera, 2005).

As a result, favorable conditions are provided for microorganisms that would recover oil products and/or oil. The success achieved in phytoextraction is mainly based on the accessibility of polluting metals in soil or their mobilization when exposed to root secretions, and the ability of plants to accumulate and translocate the metals, the tolerance to their high concentrations, and good productivity. The accessibility of metals for plants can be enhanced with various ameliorants.



**Fig. 3.** Changes in Pb, Zn, Cu and Cd levels as observed in the pure cladochaeta (*Cladochaeta candidissima*) (M. Bieb.) inhabiting the Unal tailings pond and the shingle areas of the Ardon floodplain (Ermakov et al., 2018).

The phytomass can be collected and incinerated, and the resulting ash can be buried or used as recyclable materials or fertilizers in the micronutrient deficient regions (Galiulin, Galiulina, 2008; Morozova et al., 2015; Bashkin et al., 2019).

The rapid development of indicator botany in connection with the development of biotechnologies for metal-contaminated soil remediation is either noteworthy. Taking into account the adaptive processes running, the problem of plant metal resistance and the mechanisms for its regulation within the homeostasis of separate plant communities are of particular interest. One of these mechanisms is the synthesis of biologically active SH- and SS-containing compounds (namely, metallothioneins, glutathione and phytochelatins) (Ermakov et al., 2018a).

The synthesis of this group of substances is regulated with special genes that bind a wide range of metals and promote their transfer and accumulation by organisms. Our data are indicative of some effect of a man-caused excess of metals on total glutathione levels and, to a lesser extent, on metallothionein concentrations in wild plant leaves. Apparently, the SS synthesis catalyzing occurs as a result of a complex multistep process involving the system of glutathione, phytochelatine synthase and the formation of glutathione oligomers, a group of sulfur-containing peptides - phytochelatins.

The metallothionein synthesis activation is possible as a result of a sudden increase in ions or metal complexes in the cytosol. Yet, at high levels of reduced glutathione, this process is not predominant (Ermakov et al., 2018). In addition, the leaves are less informative in relation to SS or phytochelatins than the roots. It should also be borne in mind that plants contain a range of substances (organic substances or amino acids, polysaccharides, flavonoids, etc.) that can act as chelates. The involvement of these substances in metal detoxification in wild plants requires further research works.

Phytoextraction and phytoremediation techniques are constantly being improved. Herbaceous hyperaccumulating plants are being replaced by plants with a large biomass - some trees and agricultural sunflower species, one of these woody plants being paulownia. The paulownia (Lat. *Paulównia*, the family of *Paulownia*) or the foxglove tree is a lofty (up to

15 to 20 m in height) perennial, fast-growing and foliage plant with very large leaves (from 20 cm to 50 cm) and beautiful fragrant inflorescences (up to 30 to 50 cm long) of pale purple (sometimes white) flowers. The paulownia is common in North America, Europe and Asia as a valuable gardening crop for regions with warm and humid climates.

Recently, when the searching for some alternative energy sources is carried out, paulownia gained great popularity as a raw material to be used in bioenergy as well as for soil remediation. The growth rate of the tree is ahead of all woody plants existing in the world, and as early as at the age of 8 to 9 years its wood reaches its full maturity. The leaves of the paulownia reaching a length of 20 to 50 cm are also unique in their chemical composition. They contain up to 20% proteins tasting like alfalfa or clover greens, therefore being valuable feeds in animal husbandry. They can also be used for salads. In addition, they are capable of absorbing 10 times as more carbon dioxide than the leaves of ordinary trees.

The advantages and disadvantages of the phytoremediation technique are summarized in table 7.

*Table 7. Advantages and disadvantages of the phytoremediation technique*

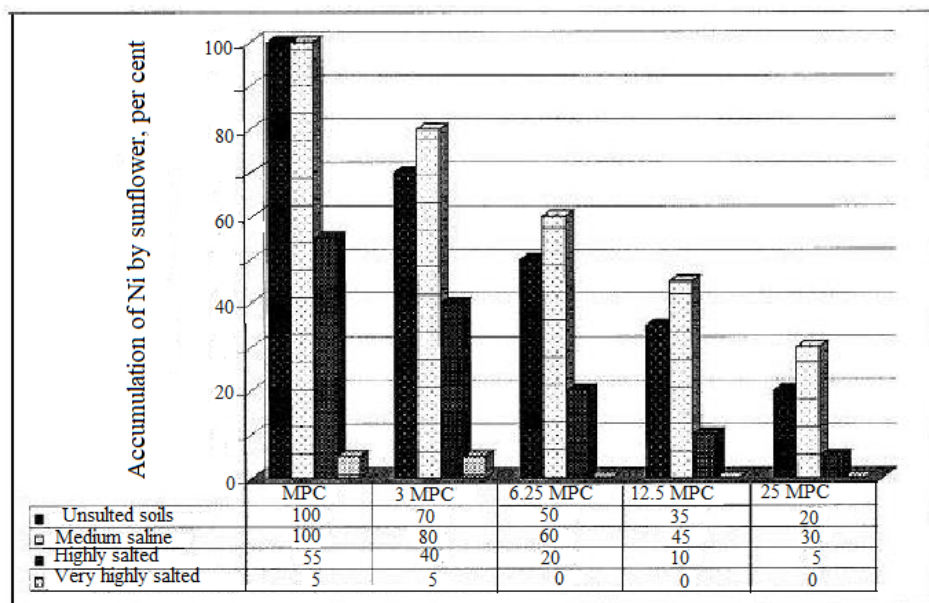
<b>Advantages</b>	<b>Disadvantages and limitations</b>
Applicability to a wide range of organic and inorganic compounds	In most cases, the method is effective for eliminating surface soil pollution within the root zone of phytoremediation plants
Applicable both in-situ and ex-situ on water or soil substrates	Decontamination of a polluted ground can take several years
In-situ application reduces soil and landscape damage as compared with the conventional cleaning methods	This method is mainly used for decontamination of environments exhibiting low or medium pollutant levels
Reduced amounts of waste buried in landfills	Problem of the contaminated plant biomass disposal arise
In-situ application reduces further spread of pollutants with water and/or air	The climatic conditions represent a limiting factor
No expensive equipment or special training of personnel is required	Introduction of plant species usually growing in other areas can disrupt the biodiversity
Potential energy stored in plant biomass can be used to produce conventional kinds of energy	Control of the contaminated plant biomass combustion/utilization is required

*Source: Andreeva et al., 2009*

The estimated CO<sub>2</sub> absorption by paulownia reaches 140 t/ha/year. Currently, some more frost-resistant clones of this plant have been obtained whose introduction is carried out by a Ukrainian company

“Paulownia Clone in Vitro 112” (Van Straalen, Denneman, 1989; Kudrik, Kudrik, 2019; Paulownia, 2019).

A number of sunflower species are very effective in terms of metal phytoextraction from soil. When growing the calendula, the lupine or the sunflower, the latter one turned out to be the most effective extractor of cadmium and/or copper (Stepanova, Nashivochnikova, 2019). In other experiments, when cultivating sunflower on saline metal-contaminated soils, a high resistance of this plant to both salinity and high metal concentrations has been determined. At the same time, metals do not accumulate in the seeds, i.e. the plant does not lose its agricultural value at the sunflower being processed into oil (Fig. 4) (Pisarenko, 2009).



**Fig. 4.** Decrease in nickel levels in soils with various salinity degrees when growing the sunflower

Source: Pisarenko, 2009

Again, a special and quite separate problem is arising here, namely what to do with the pollutant next? That is, whether this involves disposal of the cleaning final products or destruction of toxic substances extracted from the environment. They should not be simply stored as this again results in a secondary pollution of the environment. Thus, they should be subjected to industrial processing, reuse or final degradation to the stage of non-toxic compounds. Also, one can apply thermal decomposition

(incineration of waste at 1000°C or pyrolysis used as recycling methods followed by the reuse of the resources obtained).

First of all, there is a problem of “garbage”, i.e., household waste. Apparently, when developing a strategy for pollutants control, two principles are to be followed: 1) do not create industries that would violate relatively intact natural biogeochemical cycles of chemical elements, 2) give priority to techniques suggesting closed cycles with minimal introduction into natural processes. In both cases, it is required not to go beyond the known migration cycles of substances that would ensure the comfort for organisms and normal functioning of the ecosystems (Ermakov et al., 2015).

#### **4. CONCLUSION**

The above data reflect the up-to-date ecological state of the biospheric taxons and the current problems of biogeochemical regulation. As far as the clarkes of the chemical elements present in soils are concerned, we should note their relative inconstancy. First of all, there are many causes for variations in their chemical composition including a wide variety of soils and parent rock materials. Then, the factors of zoning, the area of distribution, the various conditions of soil formation, the moisture regime and a lot of other ones can play some role.

At present, a number of researchers have considered the problem of unification of the average levels of the “clarkes” of chemical elements present in soils both in separate countries and worldwide not merely methodically difficult but also far from being solved. Nevertheless, some preliminary attempts at its solution are being made in varying degrees with respect for a wide range of chemical elements. In practice, they are required to solve some environmental issues and/or evaluate the pollution degree and the potential danger of the areas polluted.

The levels of biologically active macro- and microelements present in the environment are an important factor for evaluation of the areas biogeochemical well-being, although it must be considered in connection with their concentrations within the entire biogeochemical chain.

In a context of the technogenic evolution of the biospheric taxons, the man-caused flows of matter have become comparable to the natural ones in some cases. The pollution of the habitat of organisms with toxic substance causing both the short-term and the long-term effect is turning threatening and requires immediate correction.

In order for the scale of environmental (i.e., soil, ground, water) pollution would not become irreversible and catastrophic, some changes in the environmental management strategy, elimination of the routs and sources of further pollution of the geological environment, on the one hand, and developing and implementation of methods and techniques for toxicity suppression and various geological environment elements decontamination, on the other hand, are required.

Purification technologies are an intermediate stage on the way of transforming the technosphere into the noosphere. They will be used until the mankind develops clean and closed cycle technologies.

Phytoremediation is one of the technologies to be applied at the adaptation stage of the biosphere. The advantages of the phytoremediation approach are obvious and include relatively low cost of the work to be carried out in comparison with the traditional treatment facilities; this method is safe for the environment despite some difficulties in technogenesis products disposal are emerging.

Development of waste technological disposal is one of the main tasks in this area. Toxic waste burial is a forced measure of limited use, and, to replace this potentially dangerous trend, some waste processing techniques should be developed and implemented that would include the waste concentration and conversion into an inactive form suggesting its secondary use in closed cycles.

The waste coming from various industries (sewage, tailings, sludge, dumps, settled matter, etc.) is a consequence of using imperfect technologies that must be eliminated as soon as possible and replaced with more advanced ones including closed cycles.

The entire industrial production system established requires its replacement so that it became the waste-free or the low-waste one

through using comprehensive recycling or had environmentally safe and acceptable waste disposal levels.

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