THEORETICAL STUDIES CONCERNING RESIDUAL SOIL POLLUTION BY HEAVY METALS

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Abstract: The paper describes a series of theoretical aspects concerning residual soil pollution by heavy metals. Heavy metals, unlike organic and radionuclide pollutants, are considered to be the most persistent/resistant polluting substances in the soil, displaying a tendency for accumulation. The behavior of heavy metals in the soil depends on the physical and chemical properties of the soil, as well as on their origin and source. Knowledge of the properties of heavy metals is very important, having in view the necessity of applying isolation measures for a contaminated site.

Keywords: soil, heavy metals, residual pollution

1. INTRODUCTION

As an ecosystem, the soil fulfills a series of very important functions (Figure 1), such as [1-5]:

- The ecological function:

• it contributes to regulating the composition of atmosphere and hydrosphere by the contribution of the soil to the chemical elements' circuit and the contribution of water to the environment;

• it contributes to maintaining the stability of the relief and to protecting deep layers of the earth's surface/crust;

• it contributes to the reduction of sudden variations of the soil's characteristics, with favorable effects for plants;

• it contributes to filtering various polluting substances and preventing phreatic waters from contamination;

• it contributes to cleaning the environment due to the self-cleaning process and to neutralizing polluting organic substances and pathogenic micro-organisms reaching the soil;

• it contributes to the genetic protection of some species of micro-organisms because soils represent their habitat;

- The economic function:

• it represents the main means of production in agriculture – food products and some agro-industrial raw materials;

• it constitutes the major method of production in forestry;

• it is a source of nutritious elements for plants, among which 16 are essential – carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, sulfur, calcium, magnesium, manganese, iron, copper, zinc, boron, chlorine, sodium;

- The energetic function:

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• it contributes to the accumulation of chemical energy resulting from the photosynthesis process, which is partially found in the humus;

• it supports the gradual discharge of energy resulting from the process of humus mineralization, with beneficial effects for the soil activity;

- The technical-industrial function:
  - • it performs the role of infrastructure for various constructions, roads, highways, aerodromes etc.;
  - • it is the environment used for installing subterraneous cables and ducts;
  - • it serves as raw material in industry (clay, sand, loam etc.).

Metals are part of the composition of numerous minerals, such as magmatic rocks, crystalline and metamorphic rocks, sedimenting and sedimented rocks etc. Metals can be found in the soil under various forms associated with mineral and organic components of the solid phase [2, 3, 6-8].

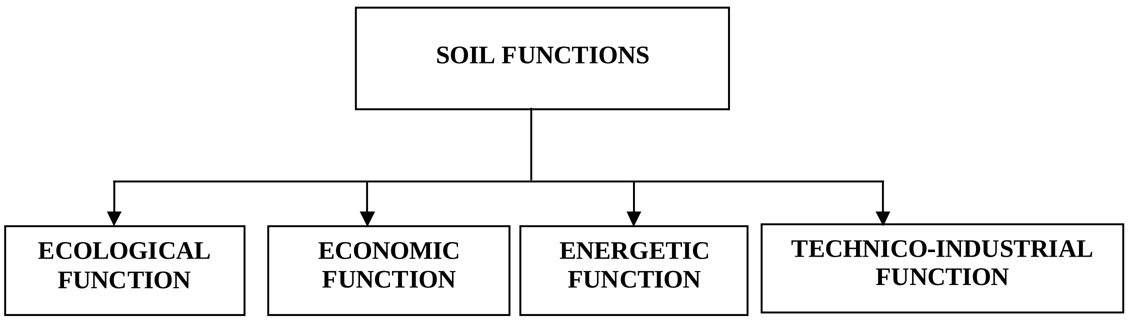

Fig. 1. Soil function [4-7, 9].

Particles in the soil's composition generally have density levels lower than 2.65 g/cm^3, with the exception of heavy metals which have density levels higher than 6 g/cm^3. Some heavy metals, such as copper, manganese, iron, cobalt, zinc, or molybdenum are essential for the development of flora and fauna, while others, such as cadmium, uranium, thallium, lead, chrome, selenium, mercury and arsenic have a toxic effect on the environment. Their toxicity level rises when the metals concentration in the soil rises, too, and the retention time generally lasts for a long time. Thus, heavy metals with concentration levels in the soil higher than 0.1 % become toxic for plants, altering the structure of the plant community in a polluted habitat. There are plants which can adapt to and tolerate high metal concentration levels (metallophytes), and there is a limit level for each plant [6, 9-11].

Table 1 presents the characteristics of heavy metals which contribute to the development of flora and fauna, high concentration levels can deteriorate flora and fauna [9, 11-13].

Table 1. Characteristics of heavy metals which contribute to the development of flora and fauna [9, 11-13].

Name	Forms of metal in soil	Distribution in soils on Earth	Distribution in soils on Romania	Toxicity to plants	Toxicity to animals
Cobalt	Association with clay minerals; Association with oxides and hydroxides of Fe and Mn; High affinity for organic matter to formation of complexes with different types of ligands	Medium content of total Co is estimate to 8 ppm	Medium content of total Co is estimate to 6.5 ppm	In excessive amounts Co is highly toxic to plants. Chlorosis and necrosis of leaves followed by drying the whole plant	In excessive amounts Co is moderately toxic to animals
Cooper	Association with clay minerals according to their absorption capacity and pH of the environment. In organic soils and bioaccumulation horizon of mineral soils, Cu organically bonded is preponderantly	Medium content of total Cu is estimate to 20 ppm.	Medium content of total Cu varies between 20 and 30 ppm.	In toxic concentrations Cu can alter the permeability of cell membranes and causes their break.	Chronic poisoning of animals by accumulating in toxic amounts in tissues and in liver especially
Manganese	Association with mineral and organic part of soil	Medium content of total Mn is estimate to 850 ppm	Medium content of total Mn varies between 850 and 1000 ppm.	Mn toxicity occurs on soils with pH values < 5.5.	Large amounts of Mn in food may reduce intestinal absorption of Fe by inhibitor effect.

Molybdenum	Association with compound that include primary and secondary minerals (clay minerals) and combination with organic matter	Medium content of total Mo is estimate to 2 ppm	Medium content of total Mo varies between 0.22 and 4.62 ppm.	Plants can accumulate significant amounts of Mo without being affected	Mo toxicity to animals is known as molybdenosis
Zinc	Association to water-soluble forms, present in soil solution. Association to strong forms retained into aluminosilicates structure, where Zn can be released by alteration	Medium content of total Zn is estimate to 50 ppm	Content of total Zn from the upper horizon of the main soil types varies between 11 and 97 ppm..	Negative effect on the absorption and use of other nutritional elements	Rarely meted

2. RESIDUAL SOIL POLLUTION WITH HEAVY METALS

Soil pollution can gave as an effect the physical, chemical, biological and radioactive degradation of the soil. Additionally, pollution can be produced by a series of substances which affect the soil for a longer or shorter time period [1-4].

Long-time effect pollution is known as residual pollution and refers to the period in which the noxious/harmful substances persist or remain in the environment, especially in the soil and in sediments, degrading them to the extent that they are no longer recoverable or restorable. The residues from these substances accumulate in the soils, waters and vegetal products and can even continue to exist there after 10 years or even more (such as pesticides and heavy metals) [5, 8, 10].

The analysis of soils and sediments in our country showcased the presence of maximum concentration levels of 9.543 ppm of substances with high soil remanence, the approved limit established by international environment committees being of 0.100 ppm [5, 9].

The determination of the remanence time in the soil or in sediments depends on the chemical nature of the substances and on their capacity to undergo change by metabolism. In other words, the measurement of remanence in the soil or in sediments depends on the resistance of the chemical molecule to metabolism and on the biodegradation capacity and degree [11, 13].

Substances with long-time presence in the soil and sediments are produced by human activities, such as [3, 6, 11, 13]:
- agriculture – the treatment of agricultural crops using chemical substances (pesticides, insecticides, herbicides etc.), watering crops using waters from contaminated rivers;
- mining – activities contaminate the soils and underground waters in waste storage areas;
- industry – activities which contaminate the soil and sediments with organic and inorganic substances like hydrocarbons resulting from oil, detergents, salts, or nitrates extractive and processing industries.

Table 2 presents the sources from the socio-economic system which generates heavy metals [5, 9, 13].

Table 2. Sources from the socio-economic system which generates heavy metals [5, 9, 13].

Source of pollution	As	Cd	Cr	Cu	Pb	Hg	Ni	Zn
Mining and ore processing	yes	no	no	yes	no	yes	no	yes
Metallurgy	yes	no	yes	yes	yes	yes	yes	yes
Chemical industry	yes	no	yes	yes	yes	yes	no	yes
Alloys industry	no	no	no	no	yes	no	no	yes
Paint industry	no	no	yes	no	yes	no	no	yes
Glass industry	yes	no	no	no	yes	yes	no	no
Cellulose and paper industry	no	no	yes	yes	yes	yes	yes	no
Hides tanning	yes	no	yes	no	no	yes	no	no
Dyeing and textile printing	yes	yes	no	yes	yes	yes	yes	yes
Chemical fertilizer industry	yes	yes	yes	yes	yes	yes	yes	yes

Chlorinated alkanes industry	yes	yes	yes	no	yes	yes	no	no
Oil refining	yes	yes	yes	yes	yes	yes	no	yes
Burning coals	yes	yes	yes	yes	yes	yes	yes	no

When the pollutant interacts with the environment (soil, water, air), the following phases can be detected [5, 11, 13, 14]:

- the pre-impact phase – the appearance of the pollutant and the evolution of the environment, the duration of this phase being variable;
- the impact phase – the proper interaction between the pollutant and the environment, a process which generates the stress and the risk depending on the nature and intensity of the pollutant. On the one hand, substances which pose risk display a specific action (for example, hexavalent chromium is highly toxic, while trivalent chromium has much lower toxicity levels). On the other hand, chemical, biological and physical pollutants show a synergic action with natural pollutants, leading to the installation of environmental degradation processes. The duration of this phase is also variable;
- the post-impact phase – the continuation and finalization of the interaction between the pollutant and the environment, a phase which is also variable.

Figure 2 presents the residual pollution phenomenon [5, 13, 14].

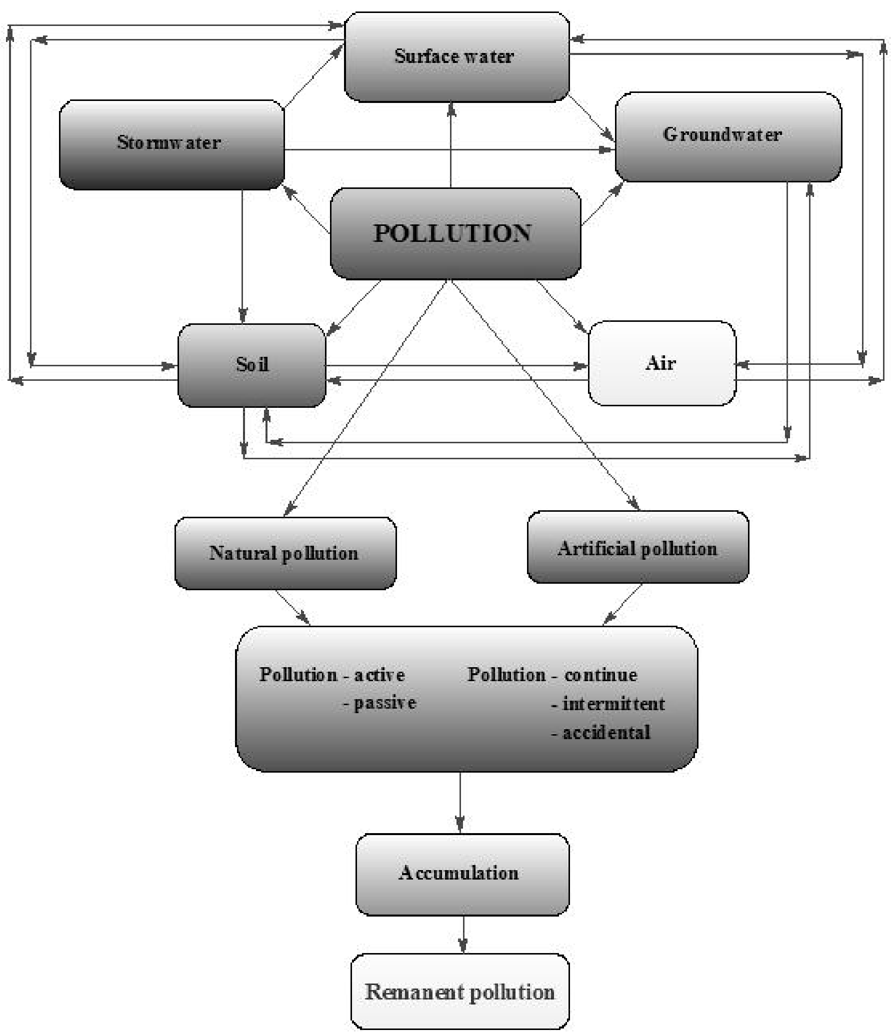

Fig. 2. Schematic representation of residual pollution phenomenon [5, 13, 14].

Once heavy metals penetrate the environment, they undergo absorption by the various life mediums (soil, water, air) and also by the organisms in the respective ecosystems. Thus, heavy metals in the air can be absorbed/ inhaled directly or can reach the soil surface by means of rain. Plants absorb the dissolved metals from the contaminated soil. Plants contaminated with heavy metals represent food/ nourishment for the human beings and animals. On the other hand, pollution can take place by infiltration in the underground waters, which subsequently transfer the pollutants to surface and drinking waters [7-13, 15].

The presence of high remanence substances in the soil and in sediments leads to the occurrence of the phenomenon entitled residual pollution, a type of pollution which can be classified as follows (Table 3) [9, 11, 13, 15]:
- physical residual pollution;
- chemical residual pollution.

Table 3. Types of residual pollution and their characteristics [9, 11, 13, 15].

Type of residual pollution	Causes	Effects	Persistence in soil and sediments
Pollution chemical residual	Presence in soil and sediments of the chemical substances with low degree of metabolizing: pesticides; solid waste from mining that contain heavy metals in high concentration; oil	Depleting of soil and sediments of humus and nutritive elements	More than 18 months – organo-chlorinated pesticides, pesticides that contain heavy metals
			Up to 18 months – urea compounds, triazines
			Up to 12 months – amide derivatives, benzoic acid derivatives
			Up to 6 months – phenoxyacetic herbicides, toluidines
			Up to 3 months – carbamide herbicides
Pollution physical residual	Practice of aggressive agriculture	Loss of the fertile soil	The Chernobyl explosion caused ground water contamination with an immense amount of radioactive waste, so that the surrounding soil is impractical for agriculture or other activities after 25 years from accident
	Occupation of large areas of land with the waste dumps, tailing dams and other facilities related to mining activities	Destruction of soil structure due to the improper use	
	Improper disposal of radioactive waste resulting from processing of the uranium ores		
	Improper disposal of spent nuclear fuel and waste resulting from decommissioning of nuclear reactors	Compaction and landslides	
	Nuclear accidents (eg., Chernobyl explosion)		

Substances with the highest risk for flora, fauna and humans are represented by heavy metals. The use of these chemical substances on a large scale and in large or repetitive quantities has negative effects on an ecological level, thus determining major alterations of ecosystems [8, 9, 13].

Heavy metals are characterized by the following physical parameters: atomic mass, melting point, boiling point, metallic beam [13, 15].

Knowledge of the properties of heavy metals, such as adsorption, complexation and precipitation is essential taking into account the necessity of applying securing/isolation measures for contaminated sites. By means of these processes inorganic pollutants can be transformed into non-toxic compounds or highly toxic compounds [7, 9, 10, 12].

Absorption is defined as the phenomenon by means of which pollutants reaching the soil are fixed on the surface of solid particles from the soil's composition, and affinity represents the selective adsorption of metals by the soil, depending on the soil's and metals' properties [7, 8, 13].

Complexation occurs when a metallic cation interacts by means of covalent bonds with an inorganic anion or an organic or inorganic group. The stability of the compounds formed in this manner is directly proportionate to the pH soil value [8-10, 13].

Precipitation is the phenomenon by means of which metals from the solution are deposited at the interface of the soil's solid particles, a new solid substance thus being accumulated. The precipitation/retention of heavy metals in the soil depends on the pH of the soil, of interstitial water and the solution's concentration levels in metals [7, 8, 13, 15].

Of major importance for the solubilisation of heavy metals in the soil is the redox reaction and potential/reduction. The transportation of heavy metals in the soil is performed by means of the liquid phase. Additionally, it can also be realized, on a smaller scale, by means of plant roots and living organisms from the soil. Mechanical works of the soil can represent circulation sources for heavy metals from the soil surface to deeper layers [8, 9, 12, 15].

A certain quantity of metal is absorbed by the plant from the soil, in normal conditions, as a nutrition element (Fe, N, Cu, Zn) or as a passive element (Pb, Cd). High concentrations in the soil – resulting from pollution – determine, depending on the chemical features of soils, the absorption of high levels in plants, sometimes reaching toxic levels with negative effects on plant growth and crop development as well as with undesirable consequences for the other environmental factors [7, 9, 11-13, 15].

The effects of pedogeochemical and biogeochemical circuits of heavy metals in nature are visible most of all in heavy polluted areas as a result of industrial emissions [7, 13].

Heavy metals proceed especially from highly industrialized areas and urban environments. Soil pollution with heavy metals can also arise from treating soils with fertilizers. These substances contain arsenic, cadmium, chrome, copper, lead, nickel, mercury and zinc [4, 8, 11, 13].

The effects of heavy metals upon the soil depend on their solubility in the soil. Heavy metals have the capacity to easily change their valence, forming hardly soluble hydroxides, and showing affinity for the creation of sulphides and complex combinations, which makes them easily retainable by the soil [4, 9, 11, 13, 15].

The transport of heavy metals in the soil is carried out in liquid or suspension form, either by means of plant roots or by connecting with microorganisms in the soil [4, 13].

Coarse, sandy and acid soils have a reduced capacity of retaining heavy metals, so these are easily absorbed by plants [11, 13].

Clay soils preserve large quantities of pollutants. The accumulation of heavy metals can be realized by the precipitation of certain chemical compounds, by association with organic molecules, by co-precipitation together with iron or manganese oxides in the form of carbonates, as well as by integration in crystalline minerals or by a series of complex chemical and biological interactions which include: oxidation-reduction reactions, precipitation and solubilization, volatilization, surface and solution complexation, bio-accumulation, bio-percolation etc. [2, 8, 12, 15].

The negative effects of heavy metals in the soil are [7, 8, 11, 13]:
- high toxicity impact on both flora and fauna;
- a relatively low selectivity capacity;
- long-term persistence (from a few months to a few years) because they have a reduced biodegradability level;

- they spread on great distances and are incorporated in the biomass.

Table 4 presents the approved maximum concentration levels for heavy metals in the soil in some European countries [8, 9, 11].

Table 4. Approved maximum concentration levels for heavy metals in the soil in some European countries (mg/kg dried substance) [8, 9, 11].

Metal	Directive 86/278/ EEC	Country						
		Austria	Germany	French	Greece	Italy	Holland	Spain
Cadmium	1 – 3	1 – 2	1.5	2	1 – 3	1.5	0.8	1 – 3
Cooper	50 – 140	60 – 100	60	100	50 – 140	100	36	50 – 210
Plumb	50 – 300	100	100	100	50 – 300	100	85	50 – 300
Zinc	150 – 300	200 – 300	200	300	150 – 300	300	140	150 – 450

Table 5 presents shows the approved maximum concentration levels for heavy metals in the soil, according to Order no. 161 from February 16, 2006, *Soil chemical quality elements and standards.*

Table 5. The approved maximum concentration levels for heavy metals in the soil [16].

Quality indicator	Unit of measure	Approved maximum concentration levels
Cadmium	mg/kg	0.8
Nickel		35
Chromium		100
Cooper		40
Plumb		85
Arsenic		29
Zinc		150
Mercury		0.3

3. CONCLUSIONS

The degree of soil pollution depends on the geological nature of the soil, on the porosity and permeability of component rocks, as well as on the hydrographical network.

Residual chemical pollution is caused by the presence of chemical substances with reduced metabolisation levels.

Soils respond differently to the same degree of contamination by heavy metals, depending on their properties, and each soil type is characterized by a specific degree of vulnerability to pollution by heavy metals.

Such a type of pollutant, namely the category of heavy metals, is extremely dangerous because of its long-term remanence in the soil, and because they are taken over by plants and animals. These toxicity elements go hand in hand with the possibility of combining heavy metals with minerals and oligo minerals which are thus blocked, so organisms are deprived of these elements which are indispensable for life. The property of heavy metals to accrue in vegetal and animal organisms, together with the pathology they determine justify the interest rate for such pollutants.

European standards for chemical soil quality in countries like Austria, Germany, France, Greece, Italy and Spain are much more accessible than the ones in Romania or the Netherlands, as follows:
- in case of cadmium, Directive 86/278/EEC established a maximum level/limit within the range of 1 and 3 mg/kg, and the most accessible limits are set for Greece and Spain;
- for copper, Directive 86/278/EEC established a maximum level/limit within the range of 50 and 140 mg/kg, with most accessible levels for Spain;

- for plumb, Directive 86/278/EEC instituted a maximum level/limit within the range of 50 and 300 mg/kg, the most accessible limits being set for Greece and Spain;
- concerning zinc, Directive 86/278/EEC ascertained a maximum level/limit within the range of 50 and 300 mg/kg, the most accessible limits being established for Spain.

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