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ECOLOGICAL RISK ASSESSMENT OF HEAVY METALS IN SOILS AND SEDIMENTS: A REVIEW

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Heavy metal contamination is the type of pollution that causes some of the most significant adverse effects to animal, environmental and human health. High concentrations of heavy metals in water and sediments result in several environmental impacts. It can reduce the fertility and productivity of the soil, it may affect plants development and a further transfer into the food chain may occur, exposing thus the consumers to health risks. Depending on the specific conditions, these metals can accumulate up to a toxic concentration level that can lead to significant ecological damage. In this regard, several methods have been developed to assess the ecological risk posed by heavy metals in soils/sediments, methods related to the calculation of different pollution indices such as: the *geo-accumulation index*, the *potential ecological risk index*, the *risk assessment code*, the *enrichment factor*, among which the first two indices have been the most widely applied. This paper briefly describes the available methods developed for predicting the potential ecological risks of toxic metals in soil/sediments systems, highlighting the importance of their application in characterizing the effects of natural and anthropogenic impacts on ecological resources.

Keywords: ecological risk, heavy metals, index of geo-accumulation, the potential ecological risk index, soil/sediments.

INTRODUCTION

Tremendous amounts of industrial waste, mining by-products, chemical fertilizers, pesticides and other toxic chemicals resulted from different industrial and agricultural activities pose serious threats to food security, food safety and human health, on a global scale[1]. Among toxic compounds, heavy metals (HMs) such as cadmium, lead, copper, chromium, nickel, zinc, arsenic and mercury had emerged as a global environmental issue due to their toxicity, persistence, non-biodegradability and bioaccumulation nature in several media (*e.g.*, soil, plants, sediments), with further transfer through the food chain[2,3]. This can have serious consequences for the health of the human population, affecting the reproductive system, inducing cardiovascular diseases, skin allergies, nutritional deficiencies, endocrine disorders, tumors, neurological diseases, and even carcinogenic risk[4,5].

HMs may result from both natural (volcanic eruptions, weathering of soils and rock, forest fires) and anthropogenic (metal plating plants, mining operations, fertilizer industries, tanneries, battery manufacturing, paper industry and pesticides, urban runoff, energy production, road traffic) sources[4,6,7]. Nowadays, there are concerns regarding the pollution of urban and agricultural soils with metals, which typically contain increased levels of pollutants compared to rural soils or background values[8,9]. For example, Xiao R. *et al.*[10] reported that agriculture and industry strongly increase HMs pollution in agricultural soils, particularly in soils around cement and galvanizing factories. Spahić M.P. *et al.*[11] reported increased concentrations of Zn and Fe in soil samples near a welding factory. Li J. *et al.*[12] found high levels of Pb contamination in the topsoil around a lead-smelter. This could mean that the soil surface is a favorable site for the storage of heavy metals and their subsequent transfer to plants by absorption together with water through the roots, and lastly by the vascular system[6]. The occurrence of metals in soil damages its structure and fertility with further negative effects on plant growth and development[5].

HMs may also accumulate in water bodies affecting different aquatic organisms with the possibility to enter into the food chain, exposing consumers to health risks[3]. It is important to note that sediments play an important role as a habitat for aquatic organisms to growth, develop and settle in an ecological system. At the same time, sediments are the final reservoir for the majority of metal contaminants in riverine ecosystems. Thus, sediment contamination is one of the indicators for predicting potential ecological risks in the aquatic systems[13]. In this regard, analyzing the data of Cd, Fe, Co, Mn, As, Pb Cr, Cu, Zn and Ni levels in aquatic sediments from India from 1979 to 2017, Kumar V. *et al.*[13] stated that the mean value of Zn, As, Cu, Cr, Pb, and Co in the sediment from India exceeded the range of Australian Interim Sediment Quality guidelines. Kalani N. *et al.*[3] measured the quantities of As, Cr, Pb, Cd, and Ni in water and sediment samples taken from Gomishan (a wetland located in Golestan, Iran). According to their results, Gomishan wetland had a moderate risk of HMs contamination, the authors indicating that a continuous monitoring of this area should be performed.

Overall, in light of the aforementioned, this review focuses on the toxic effect of heavy metals adversely influencing the agricultural and aquatic ecosystems (plant, soil, aquatic organism) and human health. Special emphasis will be given on the illustration of available models for estimating ecological risk of HMs in soils/sediments. The information from our paper will offer an insight into understanding the hazardous effects of environmental toxicants, particularly on living organisms.

HEAVY METALS IN THE ENVIRONMENT

Heavy metals along with pesticides are at the top of the list of environmental toxic substances that threaten nature[6]. Excessive accumulation of heavy metals in urban soils and aquatic biota may damage the soil and aquatic ecosystems. Since HMs are available in different forms, they may accumulate in plants and aquatic biota, leading to toxicity issues. HMs are important pollutants in agricultural environments, thus affecting food quality and human health[14,15]. For instance, regular exposure to individual or mixture of HMs may cause acute and chronic diseases such as osteoporosis, epilepsy, headache, coma, cardiovascular diseases, skin allergies, neurological diseases, reproductive disorders, lung cancer, renal dysfunction and liver problems (Figure 1)[4,6].

Although some heavy metals are essential elements for several organs of both plants and humans, they become toxic when their concentration exceeds the recommended level. Most of the toxic metals are cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As), copper (Cu), chromium (Cr) and nickel (Ni)[16]. International Agency for Research on Cancer (IARC) classifies cadmium in the first category as carcinogen and lead as being probably carcinogenic to humans[9,17]. Agency for Toxic Substances and Disease Registry (ATSDR) listed As, Pb, Hg and Cd in the top ten hazardous substances responsible for the greatest risk to human health[17].

Cadmium is not an essential element having no biological function, but nevertheless tends to be 2 to 20 times more toxic compared to other metals, even at low concentrations[18]. Cadmium is very toxic to kidneys and causes bone mineralization by its interaction with calcium leading to osteoporosis[19].

Copper is an essential trace element for all organisms especially to brain function (up to 12 mg per day), although it can be toxic at extremely high levels (the normal value in soil is 20 mg/kg)[6,14].

Lead, similar with cadmium, is not an essential element for living organisms being used for the production of batteries, paints, cosmetics and metal products. It is very toxic to plants, animals and humans. The concentration of Pb that is naturally present in soil is about 50 mg/kg[18,19]. In the presence of Pb stress, plant growth and seed germination are affected, damaging chlorophyll and photosynthetic processes[9].

Nickel is a naturally abundant element having an essential role in human metabolism and development of plants and microorganisms[16]. Nickel has different adverse effects on human health, being reported to be one of the most common causes of allergic contact dermatitis along with other effects such as nasal and lung cancer, kidney and cardiovascular diseases[16].

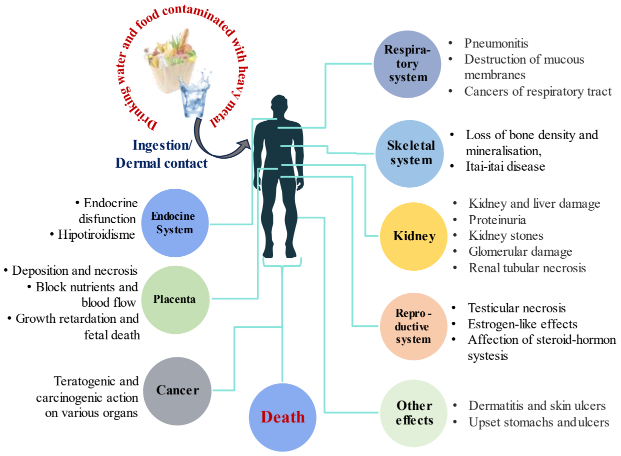

Figure 1. Effects of heavy metals on human health.

DEFINITION OF ECOLOGICAL RISK

Risk is defined as a combination of the probability of an incident (i.e., the occurrence of a hazard) and the maximum consequences that arise as a result of the occurrence of the hazard (unwanted consequence of an incident)[20]. As stated by Chapman P.M.[21], *"risk refers to a probability; a hazard refers to a possibility"*. Accordingly, ecological risk refers to the probability of occurrence of an unwanted ecological event[22]. In summary, for example, if there is a risk that a specific level of mercury in the aquatic environment will adversely affect the fish, there is a probability that this will happen. If there is a possibility that a specific level of mercury in the aquatic environment will adversely affect the fish, this is a possibility, but it remains to be established with certainty the probability of occurrence[21].

Risk assessment procedures are essentially methods and techniques for identifying, estimating and controlling risks. These procedures are used by legislative authority and/or industries to set up environmental standards and cleanup levels. In the same time, risk assessment procedures represent useful tools in providing decision support by estimating the risks of adverse effects on human health and the environment from chemicals, physical and other environmental stressors/pollutants[20,23].

The process of ecological risk assessment (ERA) is multidisciplinary and integrates knowledge from different fields such as: ecology, environmental chemistry, environmental toxicology, geochemistry, hydrology, engineering, risk management, in estimating the probability of adverse ecological impacts[22].

USEPA considers that each level of risk estimation consists of the following parts[21,22,24]:

1. Problem formulation

– description of the ecological site;

– collection and analysis of data on chemical pollutants;

– selection of pollutants affecting the ecological system (sources of potential risk –stressors);

– selection of key receptors (endpoints) potentially at risk: receptors are components of the ecosystem that are or may be affected by chemical or other stressors; grouping of species, organisms, habitats or ecosystem components on the principle of key receptors);

– identification of ecological targets and effects;

– development of a conceptual ecological model of the site.

2. Analysis phase

–- *exposure assessment* (characterization of exposure points; identification of potential exposure pathways; quantitative exposure assessment taking into account the frequency, magnitude, and duration of exposure);

– *assessment of ecological effects* (describes the relationship between the stressor and the receptor; selection of limit values from literature, establishment of toxicity reference values).

3. Preliminary risk characterization and conclusions

– risk estimation and risk analysis;

– one measure of toxicity assessment for ecological receptors is the toxicity reference values (TRVs). The reference dose estimates the daily amounts entering the body over a lifetime and assumes a threshold for toxic effects;

– hazard quotients (HQs) can be calculated by dividing the concentration of the chemical in the receiving organism (mg/kg) by its TRV value (mg/kg);

– HQs equal to or greater than 1.0 imply risk; quotients higher than 10 implies high risk; quotients less than 1.0 suggest minimal or no risk.

ECOLOGICAL RISK ASSESSMENT METHODOLOGY FOR SITES (SOILS/SEDIMENTS) CONTAMINATED WITH HEAVY METALS

The most widely applied methods to assess the environmental risk posed by heavy metals in soil/sediment are as follows:

– *geo-accumulation index* (I_{geo}) (Müller G.)[25];

– *potential ecological risk index (PERI)* (Håkanson L.)[26];

– *risk assessment code (RAC) method* (Perin G. *et al*.)[27];

– *enrichment factor (EF)* (Buat-Menerd P. and Chesselt R.)[28].

1. The geoaccumulation index method (I_{geo}). The method was developed by Muller in 1969 and was mainly applied to assess the degree of heavy metal pollution in sediments/soils with respect to natural background level as a reference. I_{geo} indicator is calculated with the following relation, Eq. (1)[29]:

$$I_{geo} = log_2\left[\frac{C_n}{1.5B_n}\right] \tag{1}$$

where: C_n - the total measured amount of heavy metal *n* in soil/sediment (mg/kg); B_n – geochemical background values of heavy metal *n*; *1.5* is a correction factor that accounts for petrogenesis effects for soil metal reference values.

The degree of pollution based on I_{geo} index is given in Table 1[15,29].

2. The potential ecological risk index (PERI) method developed by Håkanson in 1980, assesses the environmental risk of heavy metals in soil by taking into account the toxicity of the metal and its concentration in soils (Eq. 2).

$$PERI = \sum E_r^i \tag{2}$$

$$E_r^i = T_r^i \, x \, C_f^i \tag{2.1}$$

$$C_f^i = C_0^i / C_n^i \tag{2.2}$$

where: *PERI* = sum of the potential risk of each heavy metal (Risk index); E_r^i = the potential ecological hazard coefficient of heavy metal *i*; T_r^i = toxic response factor (the values can be retrieved from Håkanson[26] for each metal: Cu=Pb=Ni = 5; Zn =1; As=10; Cr = 2; Cd = 30); C_f^i = the contamination coefficient of the pollutant in soil; C_0^i = the measured heavy metal content (mg/kg); C_n^i = the background value of heavy metal content (mg/kg) – the values can be found in the literature for each metal depending on the studied area (you can check the paper of Ungureanu T. *et al.*[30] where the values for Europe soils and World soils are provided).

The E_r^i and *PERI* values are classified in Table 2 according to the system described by Håkanson L.[26].

Table 1

Standard for evaluation of soil pollution degree by I_{geo} index method

I_{geo}	**Level of pollution**	**Degree of soil pollution**
<0	0	Unpolluted
0–1	1	Slightly polluted
1–2	2	Moderately polluted
2–3	3	Moderately to highly polluted
3–4	4	Heavy pollution
4–5	5	Heavy to severe pollution
>5	6	severe pollution

Table 2

Classification of standard values of potential ecological risk index[29]

E_r^i	**Risk degree of E_r^i**	**PERI**	**Risk degreee of PERI**
$E_r^i < 40$	low	$RI < 150$	low
$40 \leq E_r^i < 80$	moderate	$150 \leq RI < 300$	moderate
$80 \leq E_r^i < 160$	considerabile	$300 \leq RI < 600$	considerabile
$160 \leq E_r^i < 320$	high	$600 \geq RI$	very high
$320 \geq E_r^i$	very high	–	–

3. The risk assessment code (RAC) method developed by Perin G. *et al.*[27]

Heavy metals in soils/sediments are distributed in different fractions with different mobility. Concentrations and chemical speciation of metals in the biotope compartments vary along with some specific physico-chemical parameters (pH, organic matter content and cation exchange capacity)[31]. For example, Cd solubility may increase in acidic soils, resulting in enhanced migration, while the mobility of Pb in soil is poor[32]. The bioavailability of metals may vary seasonally, for example their toxicity to the benthic community may be highest in autumn, when due to the decomposition of organic matter both a direct and indirect inhibitory effect may occur[33].

There are 5 mechanisms of heavy metal accumulation in soils/sediments[34]:

- *F1 – water soluble* or *exchangeable fraction*;
- *F2 – inorganic or carbonate bound fraction* (acid soluble);
- *F3 – oxidizable fraction* – bound to organic matter;
- *F4 – reducible fraction* – bound to reducible phases (iron and manganese);
- *F5 – residual fraction* – bound to silicates and residual materials.

It is desirable to identify and quantify the forms in which a metal is present in soil/sediment in order to acquire a more precise insight into the potential impacts and toxicity of metals levels in soil/sediments[14]. To determine the above mentioned fractions, the soils samples are subjected to sequential extraction methods. In this regard, the *RAC* method classifies the risk levels based on the chemical speciation of heavy metals. The majority of trace metals in soils/sediments are associated in the carbonate and exchangeable fractions[35,36]. As stated by Asmoay A.S.A. *et al.*[14] *"these fractions are considered to be weakly bounded metals that can equilibrate with the aqueous phase and thus become more rapidly bioavailable"*. Thus, in line with *RAC* method these soils/sediments exhibit a medium risk (Table 3)[35].

Table 3

Classification of *RAC* in soil/sediment[14,35]

Criteria (metal in carbonate and exchangeable fractions)	**Risk**
< 1	No risk
1-10	Low risk
11-30	Medium risk
31-50	High risk
> 50	Very high risk

According to Perin G. *et al.*[27], *RAC* can be calculated based on Eq. (3):

$$RAC = (100 \times F1 + F2)/(F1 + F2 + F3 + F4 + F5) \quad (3)$$

where *F1*, *F2*, *F3*, *F4* and *F5* are the fractions mentioned above.

4. The Enrichment Factor (EF)

The *Enrichment Factor (EF)* is an indicator that shows the degree of metal contamination in soil, being useful to assess the presence and intensity of anthropogenic pollutant deposition on the surface soil (Eq. 4, Table 4)[4].

$$EF = \left(\frac{E_S}{E_{background}}\right) / \left(\frac{R_S}{R_{background}}\right) \quad (4)$$

where E_s is the concentration of the element considered in the soil; $E_{background}$ is the content of the same element in soils worldwide; R_s is the concentration of the reference metal in the soil, and $R_{background}$ is the content of the same reference element in soils worldwide.

EF can be calculated based on normalized metal and the background value of the metal (Eq. 4). For normalization, Fe and Al are usually considered as reference elements because these metals showed the lowest levels of human contamination. The reference element is also an element *"that has a purely geological origin"* and is stable in soil[4,14].

Table 4

Classification of enrichment factor (EF) index[4]

Enrichment intensity	**Enrichment factor**
No enrichment	$EF \leq 1$
Low enrichment	$1 < EF < 3$
Moderate enrichment	$3 < EF < 5$
Relatively high enrichment	$5 < EF < 10$
Severe enrichment	$10 < EF < 25$
Very severe enrichment	$25 < EF < 50$
Extremely high enrichment	$EF > 50$

SHORT LITERATURE OVERVIEW

Asmoay A.S.A. *et al*.[14] in their study on the evaluation of heavy metal mobility in contaminated soils from Egypt (Nile Valley) stated that the soil samples were mainly polluted with As, Cd, and Cr metals according to the *EF* and I_{geo} indices. The soil samples were also subjected to sequential extraction indicating that Cd and As are mainly related with carbonate fraction, while Pb, Cr, Ni, and Cu are included in the residual fraction. Based on *RAC* results, the potential availability of As, Cd and Cr in the study area was eliminated. Hamid E. *et al.*[4] provided an interesting study on ecological risk assessment and pollution load index of some toxic elements (*e.g.*, zinc, copper, cobalt, molybdenum, manganese, and selenium) in the coastal soils of southwest Iran. According to their findings, the *EF* illustrated low levels of pollution for Zn, Cu, Co, Se, Mn, and Mo. Iordache A.M. *et al.*[37] carried out a complex study determining the contamination level of Cr, Ni, Cu, Zn, As, Pb, Cd, and Hg in the surface sediments of 19 sites in 2018 in Olt River sediments, Romania. According to the *RI* values, an intermediate ecological risk was observed at some locations. The I_{geo} for As indicated a change from moderate to strong pollution. However, the concentrations values of Ni, Cu, Zn, As, Pb, Cd, and Hg were higher compared with the national quality standards for sediments. An association between soil contamination and socioeconomic characteristics was performed by Masri S. *et al.*[38] when examining the distribution of heavy metal concentrations in soil and social vulnerabilities to soil heavy metal exposures in Census tracts in Santa Ana, California. All census tracts in Santa Ana had a risk index of >1, indicating a potential for non-cancer health effects, and almost all census tracts had a cancer risk of $>10^{-4}$, suggesting a higher than acceptable risk. The risk was mainly related to childhood exposure. Regarding the concentrations of HMs in soil, almost half of the samples polluted with Pb exceeded the California safe limit recommendation of 80 ppm for Pb in the playground soil. An ecological risk assessment of heavy metals in the soil at a former painting industry facility from Belgrade was performed by Radomirović M. *et al.*[39]. Regarding the elements distribution in soil, the most abundant metals in the study area were Fe, Zn and Pb, while the most soil samples exceeded the geochemical background values. The average *EF* values for Zn and Pb are much higher compared with other metals. Taking into account the geoaccumulation index values, the soil belongs to different classes depending on the metal type and its concentrations as follows: moderately polluted class in terms of Cr, Cd, Ni, and Hg; moderately to strongly polluted soil based on the As and Cu concentrations; strongly polluted in terms of Pb and Zn. Sur I.M. *et al.*[18] investigated the soil quality from Baia Mare area, Romania (this zone was dedicated in the past to mining and processing of ores) along with soil ecological risk. The authors noted that the concentrations of Cd, Cu and Pb in the studied areas are high, exceeding the normal values and the alert and intervention thresholds according to the Romanian legislation (Order 756/1997). Taking into account the values of ecological risk index, E_r (1.5 to 4240.4) it was observed that the highest values were recorder for Cd and Pb. The values obtained for *potential ecological risk index (PERI)* (733.9–4686) resulted in a very high risk degree, since the values exceeded the maximum *PERI* value of 600. Finally, the authors suggested the selection of appropriate technology for remediation of the area affected by metal pollution. Olatunde K.A. *et al.*[40], while investigating the potential sources and status of heavy metals in soils around the Dangote cement factory in Ibese, Nigeria, found that heavy metals concentrations were higher in the soil samples compared to the reference values and chromium exhibit the highest concentrations with an average of 11.91 mg/kg. The *Geoaccumulation index* (I_{geo}) of heavy metals showed moderate to strong pollution for Cd, moderate pollution with Pb, Ni and Cr and unpolluted with respect to Zn. Based on ecological risk index, Cd was posing the highest ecological risk of all five metals studied (Cd, Cr, Ni, Pb, Zn). Given the state of heavy metal pollution of soils around the Dangote Cement Plant, Ibese, the authors suggested a review of waste management processes at the plant and increased regulatory activities[40]. Panahandeh M. *et al.*[41] conducted a preliminary assessment of heavy metals (Cd, Cr, Cu, Pb, and Zn) contamination in the Anzali Wetland, one of the most important aquatic ecosystems in Iran. The *Geoaccumulation index* (I_{geo}) showed that of all metals, only Cd posed a moderate level of contamination, while ecological risk assessment (*PERI*) also revealed that Cd was the only metal that exhibited a potentially high risk to the environment[41].

CONCLUSIONS

Environmental contamination with heavy metals has become a serious global problem due to their anthropogenic emissions, persistence, accumulative and non-biodegradable nature and adverse effects on environment and human health.

The toxicity of heavy metals in soils and sediments depends on their potential mobility and bioavailability. Some metals induce damage to the nervous system and internal organs and even carcinogenic effects. On the other part, heavy metals may affect plant growth and development by inhibition of growth and photosynthesis, the occurrence of chlorosis, nutrient uptake deficiency and ultimately inducing plant death.

To date, several soil and sediment quality indicators and indices have been developed to integrate large amounts of raw data and to support decision makers and local administrators in developing a more effective plan for pollution control and/or prevention. In this regard, risk assessment procedures are essentially methods and techniques for identifying, estimating and controlling risks.

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