

# Chemical Assessment of Heavy Metals Contaminated Soil: A Review of Evaluation Indices

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**Abstract** Heavy metals pollution of soils resulting from anthropogenic activities such as mining, smelting, fossil fuel combustion, waste disposal and agricultural activities is an issues receiving continuous attention globally. The pollution of soils by heavy metals is a threat to basic ecosystem functions and services that are necessary to maintain food security, provision of potable water, quality health and sustainable development. The impact of heavy metals on the environment is dependent on an array of factors such as concentration of the metals in the soils, the forms in which the metals exist in the soils, the use to which the soils are put to, as well as soils and ground water chemistry. Therefore, to have a clear picture of the impact of metals' contamination of soils on the environment, it is imperative to make a thorough assessment. A crucial step towards the assessment of heavy metals' contamination of soils is to establish a baseline or natural background concentrations from which various assessment techniques can be used to quantify anthropogenic inputs. This piece, attempt a review of some chemical assessment methods used to evaluate heavy metals' contamination of soils.

**Keywords:** *metals contaminated soils, chemical assessment, bioavailability, ecosystem functions, evaluation indices*

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## 1. Introduction

The soil is one of the most valuable resources that humanity has due to the variety of services it offered. It supports plants growth and biogeochemical cycling of nutrients. It serves as habitats for both micro and macro organisms. It interacts with the hydrosphere and atmosphere, and impact the quality of water and air that contact it. It represents a transformation compartment supporting a homeostatic inter-relationship between the biota and abiotic components [1]. The soil could serves as a source, a sink, or an interacting medium for nutrients as well as contaminants (e.g., heavy metals) that impacts humans, plants, wildlife, and other organisms. Its contamination particularly with heavy metals therefore, represents a major threat to the ecosystem. Heavy metals contaminated soil may pose threat to human health due to direct uptake or transfer of metals through the food chain. Some heavy metals such as Zn, Cu, Mg, and Cr are essential to maintain growth and normal functioning of living organisms including man [2]. However, many are poisonous at higher concentrations as they tend to bio-accumulate in human bodies making them dangerous and therefore poses great health and environment risk [2,3]. Other elements such as Pb, Hg, and Cd are not essential for metabolic activities and exhibit toxic properties even at very low concentrations [3]. Heavy metals occurs naturally in

rock-formation and ore minerals and so there is a range of concentrations of these elements in soils, sediments, water and living organisms that can be considered as normal because they reflect merely background concentrations. Heavy metals pollution however, refers to cases were the contents of these elements in soils are higher than the maximum concentrations, which has potential harmful effect on the soil ability to perform its basic ecosystem functions (i.e., impairment of the soil functionality). The attendant effects could be: loss of ecosystem and agricultural productivity, diminished food chain quality, tainted water resources, economic loss, human and animal illness [4]. The impact of a given metal on the environment is dependent on a variety of factors, such as its total content, the chemical speciation, and soil characteristics. Underestimation of risk to ecosystem and human health is undoubtedly an unwanted outcome, and most countries guideline will take conservative stances to avoid underestimation. However, overestimation of risk to human health or ecosystem function means unnecessary cleaning up of sites with its associated substantial cost to industries and government [5,6]. Thus, a thorough assessment is necessary to understand the true impact of heavy metals pollution of soils on the environment. Some biogeochemical characteristics/parameters have been suggested and used to indicate soil contamination with heavy metals. These include: chemical indicators (total metal content, extractable/ leachable/available fraction, and speciation); biochemical indicators (nitrogen mineralization

capacity, fluorescein diacetate hydrolysis, microbial biomass carbon, enzymatic activities); microbial indicators (basal respiration rates, microbial biomass, microbial metabolic quotient and microbial community structure); plant indicators (seed germination, root elongation, biomass yield, uptake of metals and metal accumulation in edible parts); and soil animal indicators (evaluation of the effects of accumulation of toxic metals in body of appropriate organisms such as isopods, diplopods, and annelids; abundance and/or diversity of species in soil environment). In this piece we focus mainly on the use of chemical indicators by various authors in the assessment of the impact of metals on soils and environments. Chemical assessment of heavy metals contaminated soils usually begin with collections of samples that accurately represent soils in the problem areas, followed by analysis of metals and related soil properties such as pH, organic matter content and soil texture, and comparison of contamination/pollution quantification against regulatory standards. Some of the methods used by various authors to assess the impact of metals in soils and environments are discuss below.

## 2. Some Indices for Evaluation of Heavy Metals' Contamination in Soils

### 2.1. Contamination/Pollution Index

Lacatusu [7], distinguished between soil contamination and pollution range by mean of contamination/pollution (C/P) index. This index represents the metal content effectively measured in soil by chemical analysis and the reference obtained as assessment value for heavy metal in soil. i.e,

$$C/P = \frac{\text{Actual measurement of concentration in soil}}{\text{Target values from reference table}}$$

C/P index value greater than unity (1) define a pollution range, while that lower than unity indicates contamination range. The significances of intervals of contamination/pollution index(C/P) values according to Lacatusu are as shown in Table 1.

Table 1. Significance of C/P Values

c/p	Significance
<0.1	Very slight contamination
0.1 - 0.25	Slight contamination
0.26 -0.50	Moderate contamination
0.51 -0.75	Severe contamination
0.75 - 1.0	Very severe contamination
1.1 -2.0	Slight pollution
2.1 -4.0	Moderate pollution
4.1 - 8.0	Severe pollution
8.1 -16.0	Very severe pollution
>16	Excessive pollution

Lacatusu [7].

### 2.2. Proportion of Anthropogenic Metals

The proportion of anthropogenic metals is usually computed for each metal using the equation:

$$\text{anthropogenic metal} = \frac{(X - X_c)100}{X}$$

Where, X =average concentration of the metal in soil, and X<sub>c</sub> = average concentration of the metal in the control sample. The metal content of the control (background) sample is usually taken to represent the lithogenic metal [8]. High proportion of anthropogenic metals connotes pollution from human activities.

### 2.3. Pollution Load Index

The pollution load index (PLI) is another method use to assess heavy metal load in soils, and is defined as the nth root of the multiplications of the contamination factors, that is;

$$PLI = (CF_1 \times CF_2 \times CF_3 \times \dots \times CF_n)^{1/n}$$

where n is the number of metals,

$$CF (\text{contamination Factor}) = \frac{\text{metals concentrations in soil}}{\text{background values of the metals in soil}}$$

PLI greater than unity (1) indicates pollution while that less than unity represent no pollution [9,10,11].

### 2.4. Accumulation Factor (AF) and Enrichment Factor (EF)

The Accumulation Factor (AF) or the Enrichment Factor (EF) is another common assessment method used to evaluate how much soil is impacted by heavy metal. The Accumulation Factor (AF), measures pollution as the amount or ratio of the sample metal enrichment above the concentration present in the reference station. That is,

$$AF = [C_{\text{metal}}]_{\text{soil}} / [C_{\text{metal}}]_{\text{Control}}$$

Where C<sub>metal</sub> are the concentrations in soil and control respectively. The EF however is slightly different from the AF since it normalizes the measured heavy metal content with respect to a sample reference such as Fe, Mn, Al, or Zn [12,13]. Thus the EF is calculated using the equation:

$$EF = \frac{[C_{\text{metal}} / C_{\text{normalize}}]_{\text{soil}}}{[C_{\text{metal}} / C_{\text{normalize}}]_{\text{control}}}$$

Where C<sub>metal</sub> and C<sub>normalize</sub> are the concentrations of heavy metals in soil and in unpolluted control. The Enrichment Factor (EF) has been used to assess the degree of anthropogenic influence, increasing EF represent rising contribution from anthropogenic sources [12]. On the basis of the Enrichment Factor, five categories of contaminations are identified as follows: deficiency to minimal enrichment (EF < 2), moderate enrichment (EF 2 - 5), significant enrichment (EF 5 - 20), very high enrichment (EF 20 - 40), and extremely high enrichment (EF > 40) [14].

### 2.5. Index of Geo-accumulation (Igeo)

Another widely used index of metal contamination or pollution is the Index of Geo-accumulation (Igeo) which is based on the Muller's equation stated as:

$$I_{geo} = \text{Log}_2(C_n / 1.5B_n)$$

Where  $C_n$  is the concentration of the heavy metal in the enriched sample and  $B_n$  is the concentration of the metal in the unpolluted sample or control. The factor 1.5 is introduced to cater for the lithogenic variations in soils [15,16]. The extent of metal pollution is appraised in terms of seven contamination classes derived from increasing numerical value of the index as follows: unpolluted ( $I_{geo} < 1$ ), unpolluted to moderately polluted ( $0 \leq I_{geo} < 1$ ), moderately polluted ( $1 \leq I_{geo} < 2$ ), moderately to strongly polluted ( $2 \leq I_{geo} < 3$ ), strongly polluted ( $3 \leq I_{geo} < 4$ ), strongly to very strongly polluted ( $4 \leq I_{geo} < 5$ ), and very strongly polluted ( $I_{geo} \geq 5$ ) [13].

## 2.6. Pollution Index (PI) and Nemerow Integrated Pollution Index (NIPI)

The pollution index (PI) and Nemerow integrated pollution index (NIPI) may also be used to assess the contamination of heavy metal in soils. The PI is defined as:  $PI = C_i/S_i$ , where  $C_i$  represents the measured concentration of each metal and  $S_i$  stand for the background or control value. PI may be rated as; non-polluted ( $PI < 1$ ), low level of pollution ( $1 < PI < 2$ ), moderate pollution ( $2 \leq PI < 3$ ), strongly polluted ( $3 < PI < 5$ ), and very strongly polluted ( $PI > 5$ ) based on its numerical value [17]. The Pollution index (PI) is regarded as single factor index as it reflects only the contamination of a single heavy metal. However, heavy metals contaminations of soils hardly occur singly. Therefore, the Nemerow integrated pollution index (NIPI) was proposed to evaluate the overall pollution of metals. The Nemerow integrated pollution index (NIPI) is defined as follows:  $NIPI = [1/2(PI_{ave}^2 + PI_{max}^2)]^{1/2}$ . Where, NIPI is the Nemerow integrated (comprehensive) pollution index of the sampled area, and  $PI_{ave}$  is the corresponding average value in the single-factor pollution index, and  $PI_{max}$  is the maximum value in the single-factor pollution index. The NIPI is classed as non-polluted ( $NIPI \leq 0.7$ ), warning line of pollution ( $0.7 < NIPI \leq 1$ ), low level of pollution ( $1 < NIPI \leq 2$ ), moderate level of pollution ( $2 < NIPI \leq 3$ ), and high level of pollution ( $NIPI > 3$ ) [17]. A major drawback of the Nemerow comprehensive pollution index is that it pays no attention to the weight factor and treats every pollution factor equally. Consequently, any high value of pollution factor will result in increased composite value. Actually, different pollution factors have different impacts on environmental toxicity, degradation, and removal. Thus, different pollution factors at the same level should receive different treatment in order to increase the weight factor. It is as a result of this disadvantage, that the improved Nemerow index was developed by replacing  $PI_{max}$  of the Nemerow integrated pollution index equation above by  $PI_{max}$  [18,19]. Where,

$$PI_{max} = \frac{PI_{max} + P_w}{2}$$

and  $P_w$  is the top pollution factor of weight in all the pollution factors in the sampled area ( $C_i/S_i$ ). Pollution factor weights ( $W$ ) are calculated according to

different pollutants with varying degrees of harm to the environment and human body as:

$$W_{ik} = \frac{C_{ik} / S_i}{\sum_{i=1}^n C_{ik} / S_i}$$

Where,  $W_{ik}$  is the weight of heavy metal  $i$  at site  $K$ , the ratio  $C_{ik}/S_i$  represent the pollution index for a particular metal  $i$  while  $\sum_{i=1}^n C_{ik} / S_i$  is the sum of all the pollution indices for the metals.  $C_{ik}$  is the measured concentration of heavy metal,  $i$  at site  $k$  in mg/kg and  $S_i$  is the average assessment criterion or background value of heavy metal  $i$  in mg/kg.

## 2.7. Potential Ecological Risk Index (PERI)

The potential ecological risk index (PERI) was introduced by Hakanson [20]. This approach comprehensively considers the synergy, toxic level, concentration of the heavy metals and ecological sensitivity of the metals [21,22,23]. The method comprises a single contamination factor ( $C_f$ ), a comprehensive contamination measure called the degree of contamination ( $C_d$ ), the toxic response factor for heavy metals ( $T_R$ ), the potential ecological risk index of a single element ( $ER$ ), and comprehensive potential ecological risk index ( $RI$ ). The required equations are as follows:

$$C_f = C_M / C_R$$

$$C_d = \sum_{i=1}^n C_f$$

$$ER = T_R \times C_f$$

$$RI = \sum_{i=1}^n ER$$

Where,  $C_M$  is the measured concentration in each sampled point;  $C_R$  is the reference (or background) value of each metal in soil,  $C_f$  is the pollution of a single element factor,  $C_d$  is the comprehensive contamination factor (also called the degree of contamination),  $ER$  is the potential ecological risk index of a single element,  $RI$  is a comprehensive potential ecological risk index, and  $T_R$  is the biological toxic factor of a single element, which is determined according to "elements abundance principle" and the "element release principle" of Hakanson [20]. The standardized toxic response factors proposed by Hakanson are:  $Hg = 40$ ,  $Cd = 30$ ,  $As = 10$ ,  $Cu = Pb = Ni = 5$ ,  $Cr = 2$ ,  $Zn = 1$ . The corresponding contamination factor, degrees of contamination and the grading standards for the levels of potential ecological risk are as shown in Table 2 and Table 3.

The typical PERI method considers eight pollutants (PCBs, Hg, Cd, As, Pb, Cu, Cr and Zn), therefore there is need to adjust the grading system above to suit the numbers of metals being considered [24,25]. A modified equation for a generalized approach to calculating the degree of contamination ( $C_d$ ) was given by Abraham [25] as:

$$mC_d = \frac{\sum_{i=1}^n C_f}{n}$$

Where  $n$  is number of analyzed elements, and  $I$  is  $i$ th element (or pollutant), and  $C_f$  is contamination factor. The use of modified degree of contamination (mCd), allows the incorporation of as many metals as the analyst may be interested with no upper limit. Thus, the following grading applies for the different degree of contamination: low contamination ( $mCd \leq n$ ), moderate contamination ( $n \leq mCd < 2n$ ), high contamination ( $2n \leq mCd < 4n$ ), and very high contamination ( $mCd \geq 4n$ ).

**Table 2. Contamination factors and degrees of contamination: Categories and terminologies.**

Cf classes	Cf and Cd terminologies	Cd classes
$Cf < 1$	Low Cf/Cd, implies low contamination level	$Cd < 8$
$1 \leq Cf < 3$	Moderate Cf/Cd	$8 \leq Cd < 16$
$3 \leq Cf < 6$	High Cf/Cd	$16 \leq Cd < 32$
$Cf \geq 6$	Very high Cf/Cd	$Cd \geq 32$

Hakanson [20].

**Table 3. Grading standard for single and comprehensive potential ecological risk index**

Monomial potential ecological risk factor ER	Comprehensive potential ecological risk factor RI	Pollution level (ecological hazard)
$\leq 40$	$\leq 150$	Low
40 - 80	150 - 300	Moderate
80 - 160	300 - 600	High
160 - 320	$> 600$	Very high
$> 320$		Extremely high

Hakanson [20].

## 2.8. Metals' Mobility, Bioavailability, Bioaccessibility, and Risk Assessment

The above methods of evaluation tend to focus on total heavy metals concentrations. However, there is increasing awareness that measurement of total concentrations is a crude measure of soil quality and risk to human health. The inadequacy of total concentrations in assessment of contaminant exposure to stressors has been noted by many researchers [26-32]. While total metal content is useful index in assessing risk of a contaminated site, total metal content alone does not provide predictive insights on the bioavailability, mobility, fate and ultimate impact on the environment. Thus, it is limited in providing exact dimension of pollution.

Evaluation of soils pollutions based on chemical extraction have been developed and are based on fact that strong correlation exists between the response from a given organism or group of organisms to extraction concentration. In other word, there is a strong relationship between the chemical extract and the bioavailable fraction. Chemical extractants that have been found useful in this regards include: salt solutions ( $CaCl_2$ ,  $Ca(NO_3)_2$ ,  $NH_4Cl$ ,  $NH_4NO_3$ ), dilute acid solutions ( $HCl$ ,  $HNO_3$ ), and chelating agents (ethylenediamine tetraacetic acid (EDTA), Diethylene triamine penta acetic acid (DTPA)). Ammonium bicarbonate-Diethylene triamine penta acetic acid (AB-DTPA) and acid ammonium acetate-ethylene diamine tetra acetic acid (AAAc-EDTA) have also been used as single extractants [33-40]. These methods all involve a standardized procedure in which a solution is agitated with soil or sediment, separated from the soil matrix (by centrifugation and / or filtrations) followed by

the determination of total aqueous metal by means of spectroscopic (AAS, ICP-OES) or mass spectroscopic (ICP-MS) techniques.

The degree of contamination may also be determined by leach test, the commonest among them been the extraction procedure toxicity (EPT) test (USEPA method 1310), toxicity characteristic leaching procedure (TCLP) (USEPA Method 1311), and the synthetic precipitation leaching procedure (SPLP) (USEPA Method 1312). The procedure involves measurement of metals' concentrations in leachate from soil contacted with deionized water maintained at pH 5 (EPT), an acetic acid solution (TCLP) or a dilute solution of sulphuric and nitric acid (SPLP).

Sequential extraction is also commonly used to determine the mobile, bio-available, and stable fractions of metals in soils [36,41]. Sequential extraction (fractionation or speciation) procedures contact the solid with a series of extractants solutions that are designed to dissolve different fractions of the associated metal. A typical sequential extraction approach uses progressively stronger chemical reagents to sequentially solubilize various chemical fractions of the total metal content of the soil, and separate four to seven metal fractions, such as readily exchangeable, carbonate-bound, sesquioxides-bound, organic matter-bound and residual chemical fractions (Primarily metal ions that are incorporated in silicate structures). Such fractions are operationally defined and are based on the assumption that extracting reagents possess the ability to remove each form of the element from the soil without altering other forms of the element. Fractionation (speciation) is indeed a process of separating soils, sediments and soil component into operationally defined fractions in the assessment of contamination [42]. Such separation has been widely used in various environmental studies [30,32,43,44,45,46,47].

The study of the speciation of contaminants in the environment is important in understanding how heavy metal are retained in different component hence, their mobility, solubility, bioavailability and ultimate impacts of contaminants on human health [48]. Information that will assist in understanding the mechanism of chemical and microbial transformation, as well as development of predictive models, effective remediation and waste management are also provided by the study [42,49].

The mobility and availability of heavy metals in soils is a function of their associations with various soil components. Water soluble and exchangeable forms tend to be readily mobile and phyto-available; whereas metals incorporated into crystallize lattices of clay appear relatively immobile. The other forms-precipitated as carbonate, occluded in Fe, Mn and Al oxides or complexed with organic matter could be relatively mobile or inactive depending upon the combination of physical and chemical attributes of soil [45,50,51,45]. Several sequential extraction schemes have been developed to determine the forms of metals in soils [41,50,51,53]. But the usefulness of these schemes depends on the final use to which data acquired are put to [41,54,51,34,55].

Results obtained from the different extraction schemes may vary significantly due to differences in extraction conditions and interference from other elements and components of the soil matrix. Certain pitfalls have been associated with the use of these schemes. These include:

the limited selectivity of extractants [51,56], the incomplete removal of dissolved species due to re-adsorption or re-precipitation and the possible modification of the original oxidation state of the metal or metalloid [56-59], and the deficiency of reagent dose if metal content is too high [60]. These problems suggest that interpretations of sequential extraction data must be made cautiously. Despite these shortcomings, sequential extraction is relevant in evaluating the relative usefulness of the different forms that may be present in soils [42]. The inconsistency of fractionation results between the various extractants of a given class, and difficulties in comparison of results between different extraction scheme has prompted the Bureau Commun de Recherche (BCR), that is the European Community Bureau of Reference (now the European Community Standards Measurement and Testing Programme) to develop a three stage sequential extraction scheme with the aim of harmonizing the various extraction schemes for soils/ sediments analysis [36,61]. The BCR method has since been modified by various authors [62,63].

The BCR Method associate metals with any of the following four geochemical phases: acid-soluble phase, reducible phase, oxidisable phase, and residual phase. The acid-soluble phase consists of exchangeable metals and those bound to carbonates that can easily leach into water column. The reducible phase is that bound to Fe and Mn oxides that can be released if the soil conditions changes from oxic to anoxic state. The oxidisable phase represent fraction of metals bound to organic matter and sulphides which can be released under oxidizing conditions. While the residual phase connote the fraction of metals embedded in the crystalline structures of the soil. They are immobile and non-available to plants and other organisms over the time frames of interest. The factors that may influence the availability of metals in soils include: pH, redox potential, organic matter content, soil texture, clay content and type, and cation exchange capacity. Also, the presence of both inorganic and organic ionic species affects metal adsorption, speciation, and bioavailability through direct interaction (metal-ionic species) and indirectly via its impact on surface adsorption mechanisms.

The use of soil animals as indicators of soil pollution has been highlighted in the introductory portion. The fraction of a contaminant that is absorbed into the body of animals following ingestion, inhalation or dermal contact is referred to as the bio-available fraction. Animals such as swine, mice, primates, rodents, etc have also been used to assess bioavailability, pollution status and human health risks of contaminated soils [64,65]. However, the setbacks in monitoring health risk by animal model is that the process is slow and costly (length of time is required for the experiment to reach conclusion, time and money is spent in rearing and feeding the animals), beside, ethical issues may be associated with the in vivo assays. Simple, rapid, and inexpensive in vitro chemical assessment methods have therefore been developed as alternative measure of bio-availability. Bio-accessibility assays determine the amount of metals solubilized from the solid matrix (e.g. soil) in simulated human digestive fluids and represents the amount of metals that is potentially bio-available for absorption into the systemic circulations [65]. These in vitro model, do not attempt to reproduce settings established in vivo, but mimic key processes such

as contaminant dissolution. They are based on the premise that strong correlation exist between the in vivo and in vitro results across varieties of sampled types. Bioaccessibility assays in common use include: the solubility bioaccessibility research consortium (SBRC), In vitro gastro-intestinal (IVG), Deutsches Institut für Normunge. V. (DIN), physiologically based extraction test (PBET), and the unified BARGE method (UBM) assays [64,66,67,68]. Bio-accessibility is a limiting step to bioavailability, as ingested contaminants must first be bio-accessible before it can be bio-available. Assessment of risk based on the bio-accessible fraction may slightly overestimate health risks compared to the bio-available fraction, since not all soluble contaminants in the digestive system will necessary be bio-available, some solubilized contaminants will certainly remain unabsorbed and excreted by the body. It however provides a more accurate measure for risk assessment compared to the use of total soil concentrations and also promote the application of precautionary principle.

### 3. Conclusion

Proper assessment and quantification is required to understand the true impact of heavy metals' pollution on soil environment and human health. The pollution load index, the enrichment factor, the index of geo-accumulation, and the Nemerow integrated pollution index, as well as the potential ecological risk index are commonly used to quantify the impact of heavy metals in soil environment. These methods which are based on heavy metal content which assumed a default value of 100% bioavailability tend to overestimate exposure thereby influencing risk calculation. Therefore, the fact that a seemingly contaminated site exceeded its baseline concentration (guideline value) is not enough to conclude that such site pose significant harm and required remediation. Rather it is a call for further site-specific examination taking cognizance of the soil's characteristics such as pH, organic matter content, texture, and metal's bioavailability in the soil etc, as well as the use to which the site is to be put to. It is only after such site-specific data have been thoroughly assessed, that such site may be deemed polluted and requiring remedial action. Baseline or guideline values should be considered as initial screening values for generic quantitative risk assessment, and should be regarded as maximum soil contaminant concentration tolerable over an extended period. Also, health risk assessment should not be base on chemical assessment alone. Other forms of indicators should be used to complement it so as to reach a more reliable data that could help to guide against underestimation which is risky to ecosystem and human health. While at the same time, watchful against overestimation that will result unnecessarily cost in terms of remediation and psychological effects that such report may produce on the population.

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