

Development and Validation of a New Comprehensive Method for Heavy Metal Pollution Assessment in Soil Media

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Abstract

This study was carried out to develop and validate a new comprehensive methodology for the assessment of heavy metal pollution in soil environmental media. The models were developed to fill up the gap between the existing contamination factor indices and hazard quotient, so as to avoid discrepancies in their application. The results obtained from analysis of heavy metals (Zn, Cu, Ni and Cd) in soil samples collected from Dana steel limited dumpsite upper layer were used for the validation. The existing hazard quotient and contamination factors classify Cu under very high pollution category. The existing Pollution load and the developed hazard load index characterized the dumpsite under considerably polluted category. Discrepancy was observed in the single index classification against Zn, Ni and Cd. This discrepancy was attributed to the possible improper control area selection. The proposed methodology if utilized is capable of relieving the need for control area sampling there by eliminating biasness in the environmental quality deterioration assessment.

Keywords: Heavy metals; Hazard quotient; Contamination factors; Pollution load index; Hazard load index

Introduction

According to a continuous monitoring data collected in 118 cities in china between 2-7 years, only 3% of the urban ground water meets the basic standards of cleanliness, 64% is suffering very heavy metal pollution and about 33% is suffering moderate pollution [1]. Heavy metals pollution assessment nowadays is becoming an important task due to the increase in man-made sources of heavy metals in terms of petrochemicals, compost, pesticides, animal manures, sewage sludge, leaded paints as well as the indiscriminate dumping of wastes in landfills [2]. These heavy metals when taken up in to the body even at trace amounts are capable of accumulating gradually until they reach the toxicity limit provided that their rate of entry is higher than that of their excretion [3]. Heavy metals accumulation has shown to be detrimental to both plants and animals.in human body, for example, it is capable of causing neurological disorders, damage to the internal organs of the body and even death while in plants it shows negative effects on photosynthesis and absorption/exchange of gases [4-7].

Heavy metals risk assessment has been carried out in different media using various methods. The heavy metal contamination due to fish intake has been assessed using daily intake of metal (DIM) and health risk indices by considering the daily loading of metals into the body which depend body weight of the consumer and the relative bioavailability of the metals being studied as cited by Hassaan [8], El-Rayis et al. [9] and USEPA [10]. Heavy metals contamination assessment in drinking water has been carried out successfully all over the world using quality index method. These quality index method has proved to be a significant tool for effectively gathering a composite influence of indicators to the overall contamination [11]. Several evaluation methods have been utilized by various authors in heavy metal pollution assessment in soils and sediments: Single index factor (Pi), Nemerow's pollution index (PN), potential ecological risk index (RI), enrichment factor (EF), contamination factor (CF), geoaccumulation index (Igeo), contamination index (Cd), pollution load index (PLI) as well as hazard quotient [12-20]. Pi and CF are computed as basis for obtaining PN and PLI respectively. Igeo can be used to distinguish the effects that human activities have on the environment [21]. RI considers the toxicity of the pollutant as a means of evaluating the ecological risk, the value does

so by comparing the concentration of the pollutant with the background value. EF represents the value that assess anthropogenic influences on heavy metals in sediments, the measurement uses aluminum (Al) as a conservative element [13]. However, discrepancies are usually observed in the application of these methods due to their varying assumptions. This Study therefore proposes to develop models/classification that could be used to assess the heavy metal contamination severity in hazard quotient in a way to fill the gap between it and the existing contamination factor models. The proposed methodology was validated using the data on heavy metal pollution by Zn, Cu, Ni and Cd in top soils of Dana steel limited dumpsite.

Materials and Methods

Study area used in the validation/sample preparation and analysis

Top soils of Dana steel limited dumpsite located in Katsina state Nigeria was used in the validation of the developed condition and models. The site was the same as that reported in my previous studies. Similarly, all the collected soil Samples were prepared and analyzed using the standard flame atomic absorption spectrophotometry method as utilized in the other studies [22-25].

Existing statistical indices in use for environmental quality assessment

Contamination factor (CF): Contamination factor (CF) is also

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called single pollution index (PI). Contamination factor is the quotient obtained by dividing the concentration of metals related to the target area by reference area. Their results are mostly associated with single pollution load, while their n-root was used for integrated pollution load index. The contamination factor can be calculated through the following formula as suggested by Kumar et al. [24].

$$CF = C_n / B_n \tag{1}$$

In the above equation, C_n is the concentration of metals in the target area and B_n is the metals concentration of the reference area. CF is categorized as tabulated in Table 1.

Pollution load index: Pollution load index (PLI) is simple statistical technique used to provide comprehensive information about the metals toxicity in respective samples [26,27]. Pollution load index is usually calculated through the following formula:

$$PLI = \sqrt[n]{CF_1 * CF_2 * CF_3 * \dots * CF_n} \tag{2}$$

Where, PLI represents the pollution load index, CF is the contamination factor and n is the number of elements. If PLI < 1 it indicates that there is low pollution. while PLI > 1 indicates the presence of pollution.

Hazard quotient: The soil Hazard Quotient (HQ) is the ratio of the heavy metal concentration of surveyed soil samples to reference permissible limit and is computed using the relation,

$$HQ = C_c / C_p \tag{3}$$

Where, C_p and C_c=reference maximum permissible limit of heavy metal concentration and the concentration obtained in the sampled area, respectively.

Results and Discussion

The proposed new method

The models and classifications: The models and classifications proposed were directly analogous to the contamination factor indices and pollution load index, only that the developed models utilize Hazard quotients as the input parameters in lieu of contamination factors [28]. The developed analogous formula was termed Hazard load index to distinguish it from the popularly known pollution load index. The proposed hazard load index if used will provide comprehensive information on the pollution severity in a typical heavy metals pollution assessment. The classification as adopted and amended was presented in Table 2.

The proposed hazard load index: Similar to the pollution load index that takes contamination factors as inputs, an analogous relation

Contamination factor	Classification
CF < 1	Low contamination
1 ≤ CF < 3	Moderate contamination
3 ≤ CF < 6	Considerable contamination
CF ≥ 6	Very high contamination

Table 1: Classification of contamination factors.

Hazard quotient	Classification
HQ < 1	Low
1 ≤ HQ < 3	Moderate
3 ≤ HQ < 6	Considerable
HQ ≥ 6	Very high

Table 2: Classification of hazard quotient.

termed hazard load index was developed by adoption and amendment of the pollution load equation and was presented in equation 4.

$$HLI = \sqrt[n]{HQ_1 * HQ_2 * HQ_3 * \dots * HQ_n} \tag{4}$$

The existing pollution load and hazard indices do not provide information on the severity or extent of the contamination or pollution of an environment by heavy metals. These information is very important for planning an appropriate legislation and/or remediation measure, as such, this work propose the classification provided in Table 3.

Validation of the developed method

Contamination factors (Existing method): The contamination factors corresponding to each heavy metal in a particular soil sample was calculated and the results were presented in the Table 4. From the mean contamination factors of each heavy metal and based on the classification described we could observe that Zn and Cu are in very high pollution category, Ni falls under considerable pollution category while Cd can be considered in moderate pollution category (Table 4).

The modified hazard quotients classification: The hazard quotients corresponding to each heavy metal in a particular soil sample was calculated and the results were presented in the Table 5. From the mean hazard quotient of each heavy metal and based on the

PLI or HLI	Classification
PLI or HLI < 1	Low
1 ≤ PLI or HLI < 3	Moderate
3 ≤ PLI or HLI < 6	Considerable
PLI or HLI ≥ 6	Very high

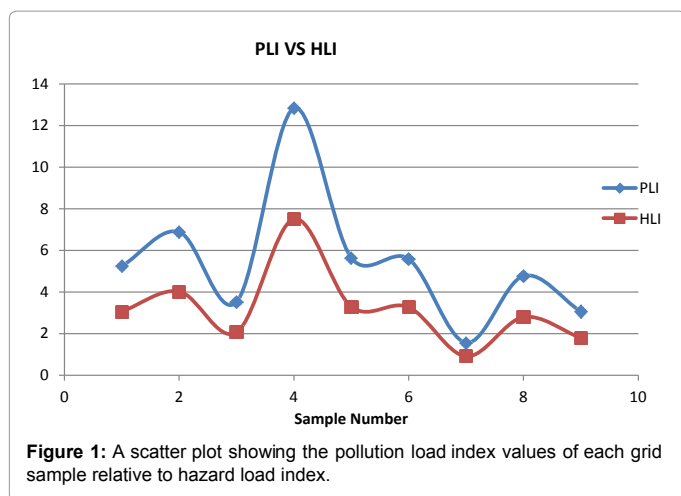
Table 3: Classification pollution load and hazard load indices.

Sample No.	CF (Zn)	CF (Cu)	CF (Ni)	CF (Cd)
1	12.77181	79.15789	4.825175	0.153846
2	18.10403	42.26316	3.594406	0.815385
3	12.63758	9.026316	1.391608	0.969231
4	19.6443	72.34211	8.111888	2.353846
5	15.0302	18.42105	2.524476	1.446154
6	9.647651	23.65789	2.867133	1.492308
7	4.671141	2.315789	0.559441	0.984615
8	10.53356	3.473684	8.27972	1.707692
9	12.38926	3.973684	1.363636	1.307692
Mean (Range)	12.826 (4.671-19.644)	28.292 (2.316-79.158)	3.724 (0.559-8.280)	1.248 (0.154-2.354)

Table 4: Calculated contamination factors corresponding to each heavy metal concentration in the studied samples.

Sample No.	HQ (Zn)	HQ (Cu)	HQ (Ni)	HQ (Cd)
1	3.806	20.05333	1.725	0.666667
2	5.395	10.70667	1.285	3.533333
3	3.766	2.286667	0.4975	4.2
4	5.854	18.32667	2.9	10.2
5	4.479	4.666667	0.9025	6.266667
6	2.875	5.993333	1.025	6.466667
7	1.392	0.586667	0.2	4.266667
8	3.139	0.88	2.96	7.4
9	3.692	1.006667	0.4875	5.666667
Mean (Range)	3.822 (1.392-5.854)	7.167 (0.587-20.053)	1.331 (0.2-2.96)	5.407 (0.667-10.2)

Table 5: Calculated hazard quotients corresponding to each heavy metal concentration in the studied samples.



classification developed in this work, we could observe that Zn and Cd are in considerable pollution category, Cu in very high pollution category and Ni falls under moderate pollution category which to a reliably higher extent agree with the existing classification in 3.2.2 (Table 5).

The pollution load index (existing) vs. the proposed hazard load index (new method)

Pollution load index was the popular index used in assessing the environmental quality deterioration due to all studied heavy metals. This index was calculated and the results were presented in a scatter plot Figure 1. The developed hazard load index was similarly used in the same study, each based on its assumptions and inputs, and the obtained calculated results were plotted in the same plot for comparison sake. Both the mean pollution load index and the mean hazard load index classified the studied site under considerably polluted category [29]. Meanwhile, observing the individual data points in the plot we could deduce that pollution load index overestimated the hazard possibly due to the improper guide on control area sampling which was evidently required in hazard assessment via pollution load index (Figure 1).

Conclusion

In this paper a new comprehensive methodology for heavy metals pollution assessment has been proposed and validated. The new method developed provides a hazard quotient grading/classification of the pollution severity in a typical soil heavy metals pollution assessment. The proposed classification if used is capable of relieving researchers of the need for control area sampling as it uses the threshold values set by a reliable legislation/organization thereby minimizing cost, time as well as errors that may be inherently encountered. In this methodology, all that is needed is to sample the soil to be studied for pollution, take it to the analytical laboratory for analysis of the heavy metals concentrations, obtain the current threshold limit of the heavy metals under study and apply the proposed equation with its classification system to obtain the status and severity of its pollution. This assessment method, however, may have some deficiencies and may require verification through more research in order to seek for the possibility of its application to cases other than soil pollution sites. The proposed evaluation method is more objective and reasonable compared to the contamination index method as even the site selected as a control in the existing contamination index classification may be polluted and may be subject to biasness. This research therefore provides an important frame of reference to the

government decision-making on environment improvement/impact assessment.

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