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Applying Various Pollution Indexes to Evaluate Heavy Metal Pollution and Contamination Levels in Soil of Karadağ Mountain from Turkey

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HIGHLIGHTS

- Heavy metal concentrations in fractions of soil and contamination.
- Pollution indices in soils formed on the volcanic material.
- Environmental risk of contamination specifiable using sequential extraction methods

Abstract

The heavy metal contents in soil fractions were determined using selective solutions and a sequential extraction procedure and then the amounts of heavy metals were calculated in these fractions of soils generated on the volcanic material of Mount Karadağ. Heavy metal status and contamination levels were determined by using pollution indices instead of comparing them with the reference rock alone. Different pollution indices were used such as Geoaccumulation index (I-geo), pollution load index (PLI), Enrichment factor (EF) and Contamination factor (CF) index. According to all indices used, there was no or very little contamination, except for RAC, and it was determined that these levels did not cause any pollution in the soil. RAC values showed a high risk especially for Cd. Although not high risk, low risk points were detected in Ni and Pb. This situation clearly reveals that in the pollution assessments, indexes that take mobile fractions into account rather than total values should be used for sensitive areas.

Keywords: Sequential extraction method; Heavy metal; Pollution indices; Karadağ

1. Introduction

Heavy metal is the term used to describe metals of the third period or higher of periodic tables, which have a physical density of more than 5g/cm^3. More than 60 metals are included in this group, such as copper, iron, cobalt, lead, chromium, nickel, cadmium and zinc. The quantity of heavy metals discharged into the environment poses major issues as a result of industrial activity's fast expansion. Environmental pollution with heavy metals may be due to both natural and man-made sources in the environment. Naturally occurring incidents such as geological weathering and volcanic eruption are the natural causes of heavy metal contamination. Heavy metal pollution of the environment is a global issue because they are difficult to extract

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from the soil. When acceptable concentration limits of heavy metals are exceeded, the majority of ecosystems are toxically affected. The heavy metals such as Cu, Pb, Cr, Fe, Zn, and Cd are often discussed in the literature regarding possible risks and occurrences in contaminated soils (Akoto et al., 2008). Because of their nature these elements are found in the earth's crust as carbonate, silicate, and sulfide, depending on stable compounds or silicates (Kahvecioğlu et al. 2004). Since the soil has a filtration feature due to its buffering capacity, it can prevent and/or delay the emergence of the effects of pollutants against the pollutants according to the water and air ecosystem. However, the issues that arise when soil deterioration results from pollution are large and complicated, and it can be difficult and costly to resolve (Kocaer and Başkaya 2003). The term "soil pollution" refers to the degradation of one or more of the physical, chemical, biological, and fertility characteristics of soils due to externally introduced or naturally occurring pollutants, as well as improper agricultural methods. Soil pollution can be named according to the type of pollutant or the deteriorated soil characteristics. Heavy metals in soils can be caused by minerals that decompose during the formation of soils (natural pollution). Heavy metal contamination can occur in soils developed on parent materials that include minerals with significant concentrations of metals (Kahvecioğlu et al. 2004). Additionally, the presence of heavy metals (artificial pollution) in the structure of compounds added to the soil for a variety of reasons may also be the cause. For example, fertilizers and pesticides that cause heavy metal accumulation, sewage waters, and treatment liquid and solid wastes are also among the heavy metal sources (Tok 1997). Natural concentrations of heavy metals are present in every soil. The chemical composition of the bedrock from which the soil is generated determines the size of a metal's background (Scazzola et al. 2003). The fundamental component of the biogeochemical system, soil, serves as both the source and the pool for a variety of contaminating species. Therefore, it is crucial in the storage and movement of pollutants (Forghania et al. 2019). Heavy metal concentrations in volcanic soils are often quite high and may exceed toxic levels. Such soils may naturally contain high levels of heavy metals due to pedo-geochemical processes (Doelsch et al. 2006). Since amorphous aluminosilicates and organo-mineral compounds produced by neoformation are abundant in soils formed on volcanic rocks, these soils have a high ability to bind heavy metals (Tanneberg et al. 2001). Heavy metals can be especially retained on aqueous oxide and oxyhydroxide surfaces of volcanic soils and subsequently absorbed due to organic complexation. Therefore, in addition to heavy metals, some trace elements nutrients for plants can also be preserved very strong and become inaccessible to plants (Tanneberg et al., 2001). Various methods can be used to evaluate the sediment enrichment with elements. The most popular ones are the pollutant load index (PLI), enrichment factor (EF), contamination factor (CF) index, and geoaccumulation index (I-geo). In addition, RAC, acid soluble fraction (F1), pollution indexes (PI), contamination degree (Cd), modified degree of pollution (mCd), can also be used to get an idea about the contamination or pollution degree. Among these indices, pollution degree (Cd), modified pollution degree (mCd), pollution load index (PLI) and pollution indices (PI) show the total effects of pollution, while others are used to reveal the individual effects of pollution elements. Determining environmental exposure hazards and comprehending the features of heavy metal contamination in soil offer crucial knowledge for both preventing soil pollution and making informed decisions about the remediation of polluted soils.

In this work, the concentrations of heavy metals in various soil fractions developed on the volcanic material of Mount Karadağ were evaluated using the sequential extraction method with selective solutions. Pollution indices were found using the results obtained and the sum of heavy metal levels in soil fractions, and the individual and cumulative effects of metals on the pollution level of the analyzed soils were emphasized.

2. **Materials and Methods**

Mount Karadağ is located in the interior belt of the Taurus Mountains, northwest of Karaman, in the semi-arid continental climate of Central Anatolia. Neogene-Quartern aged Central Anatolian volcanics in a range of volcanic mountains that run parallel to the Taurus Mountains. The yearly average temperature is 11.2 ^{o}C, and the average amount of precipitation is 340.1 mm. There is 1312.8 mm of evaporation every year. Precipitation is irregularly distributed throughout the year and mostly falls during the winter. Relative humidity is 62.5% on average. At 50 cm depths, the mean soil temperature is 13.8 °C (Anonymous 1994). Lacustrine and alluvial deposits coexist with the sedimentary formations, which are covered in an unconformable manner by this volcanism, which was active from the middle Miocene until the end of the Quaternary. Karadağ activity generated andesitic lavas of the biotite, hornblende, andesite, and hornblende andesite kinds. The topic area was examined using 1/100,000 scale soil maps (Anonymous 1992), 1/100,000 scale geological maps (Anonymous 1962), and other research in order to identify soil sample locations and collect samples. The area was then explored using topographic map sheets at a size of 1/25.000, and 15 samples were taken there in consideration of the information gathered. When selecting the sample locations, attention was given to the sort of volcanic material present in the research area. In this regard, 15 soil samples in total were gathered in Karadağ, 10 from the centrally formed volcanics in Karadağ and 5 from the andesites in Değledağ. Sample points were chosen randomly. Surface (0–20) samples were taken from 4 different locations within a 4 × 4 meter area from every sampling point. Subsequently, they were combined via subsampling and transported in plastic bags to the laboratory. A modified sequence extraction strategy was used to evaluate the amounts of Cr, Cu, Ni, Cd, Zn, and Pb (the attached forms of the heavy metals) in different fractions of soil samples. The total concentration of heavy metals was calculated as the sum of the heavy metal concentrations in each of the fractions. Many studies have described in detail the modified BCR sequential extraction method (Usero et al. 1998; Rauret et al. 1999; Ololade 2009). Metal analysis procedures were applied to the acid-extractable fraction (depending on the exchangeable and carbonate fractions), the easily reducible fraction (depending on the Fe / Mn oxide fraction), the oxidizable fraction (depending on the organic matter fraction), and the residual fraction using the BCR sequential extraction method. The pollution indices were calculated using the sum of heavy metal contents. Following air drying, the soil samples taken from the site were passed through a 2 mm sieve. A mortar grinder was used for blending soil samples homogenously before they were sieved through a 0.5 mm mesh. These samples were subjected to elemental analysis, organic matter analysis and calcium carbonate analysis. The hydrometer technique was used to determine the particle size distribution (Bouyoucos 1951). Before this process, carbonates and organic matter and salts were eliminated, and the samples were shaken in 10 milliliters of 40% sodium hexametaphosphate (Calgon) to disperse them (Gee and Bauder, 1986). The techniques of the Soil Research Laboratory (2004) were used to determine the (electrical conductivity) values of saturated soil samples. A Scheibler calsimeter (Soil Survey Manual 1993) was used to determine the $CaCO_3$ content. By titrating an acid-dichromate digestion with Fe_2SO_4, the amount of organic matter in the soil was determined (Walkley, Black, C.A. 1934). Analyses of Cd, Cu, Cr, Ni, Pb, and Zn in soil samples were carried out in an air-acetylene flame using an Agilent 5110 ICP-OES spectrometer. Metals are operated within their recommended ranges by the manufacturer. To evaluate the accuracy of the approach, an examination of the BCR-701 certified reference soil was examined and the findings were compared to the certified element concentration of the BCR. In the acid and water-soluble fraction, Oxidisable fraction, and reducible fraction, the heavy metal recovery rates in the standard reference material were found to range from 89% to 122.7%, 92.1% to 114.7%, and 71.6% to 98.9%, respectively. These rates were all regarded as acceptable. Standard items of STD DS 11 and STD OREAS 262 were also used to validate the residual fraction. Heavy metal recovery rates in the residual portion of the standard reference material varied from 91.1% to 119.4%. Each extraction phase in the BCR sequential extraction process, including the residual phase, has its own limit of detection (DL) established. Three replication samples from each stage were analyzed, and ten measurements were made. In the DL computation, the 3s/b equation has been taken into account. Where is the standard deviation of the absorbance of the blank samples and is the slope of the calibration graph for each element? DL limits ($g.mL^{-1}$) were found between 0.001-0.098 in the acid and water-soluble fraction, 0.002-0.70 in the oxidisable fraction, and 0.002-0.6 in the reducible fraction.

3. **Results and Discussion**

3.1. Shift in Soil Conditions

Values and descriptive statistics for certain physicochemical properties of the investigated soils are provided in Table 1. The average soil pH was 6.94, ranging from slight acidic to slightly alkaline. Between 72.5-261µS/cm is the range of electrical conductivity values, and no issues with agricultural salinity were noted. The mean percentage of organic matter in soil is 2.77%, with a range of 1.30 to 5.54%; $CaCO_3$ concentration ranges from 0.43 to 14.43 percent, with an average of 2.44%, and is characterized as mildly calcareous. The percentage of sand varied from 43.9 to 70.2%, the amount of silt from 6.3 to 30.0%, and the fraction of clay from 22.4 to 49.9%. These findings demonstrate that soil properties differ between sample sites. The text continues here.

Table 1. Physical and chemical characteristics of soil samples found in the study area

Example Number	**pH (1/2.5)**	**EC (µS/cm)**	**Organic Matter (%)**	**$CaCO_3$ (%)**	**Particle Size Distribution**		
					Clay (%)	**Silt (%)**	**Sand (%)**
1	7.53	238.3	4.04	0.62	26.1	25.0	48.9
2	6.71	72.5	1.80	0.47	24.9	8.7	66.4
3	6.60	81.7	1.87	0.43	23.6	6.3	70.2
4	6.70	99.0	1.77	0.58	22.4	7.5	70.2
5	6.78	182.2	2.80	0.72	37.4	18.8	43.9
6	7.10	138.3	1.41	1.75	37.4	16.3	46.4
7	7.30	215.5	4.19	2.34	31.1	30.0	38.9
8	6.94	209.1	4.29	0.74	49.9	27.5	22.7
9	6.62	261.0	5.54	0.58	31.1	28.8	40.2
10	6.55	197.4	4.72	0.74	26.1	18.8	55.2
11	6.65	80.7	1.30	0.66	34.9	10.0	55.2
12	7.19	128.1	2.06	10.92	27.4	17.5	55.2
13	7.27	131.9	1.41	14.43	38.6	15.0	46.4
14	7.11	121.9	2.16	0.82	34.9	16.3	48.9
15	6.97	104.6	2.19	0.82	28.6	17.5	53.9
Maximum	**7.53**	**261.0**	**5.54**	**14.43**	**49.9**	**30.0**	**70.2**
Minimum	**6.55**	**72.5**	**1.30**	**0.43**	**22.4**	**6.3**	**43.9**
Mean	**6.94**	**150.8**	**2.77**	**2.44**	**31.6**	**17.6**	**50.8**
ST	**0.30**	**61.6**	**1.39**	**4.24**	**7.3**	**7.6**	**12.5**

3.2. Heavy Metal Contents Detected by Sequential Extraction

Heavy metals can be found in soils in many different kinds of geochemical forms, such as changeable structure caused by iron and manganese oxides or connected with organic matter residual forms due to many physico-chemical and biological processes. Because of this heavy metals' mobility and bioavailability in soil are also affected by their geochemical forms, not just their total concentration (Bilgin et al. 2020). That is why it's critical to use a variety of extraction procedures to ascertain the percentages of mobilizable trace elements. Sequential extraction techniques (SEPs) have been developed to identify different geochemical forms of trace metals because of trace metal mobility depends on the interaction between trace metals and soil (Doelsch et al. 2008). The European Community Reference Bureau (BCR) has started utilizing a standard SEP to evaluate the results of different SEPs (Rauret et al. 1999). Table 2 displays the average distributions of heavy metals by BCR sequential extraction technique. In the study's S1 phase (exchangeable, acid and water soluble fraction) Cd was distributed between 0.032-0.106, Cr between 0.034-0.160, Cu between 0.084-1.160, Ni between 0.509-2.646, Pb between 0-0.393 and Zn between 0.380-2.724. In the S2 phase (Reducible fraction), these values varied from 0.004-0.1036 for Cd, 0.0336-1.1655 for Cr, 1.184-4.697 for Cu, 1.038-6.916 for Ni, 3.317-9.037 for Pb, and 3.414-15.161 for Zn. In the S3 (Oxidisable fraction) stage, it varied from 0.000 to 0.1069 for Cd, 1.48 to 14.939 for Cr, 2.690 to 4.720 for Cu, 1.665 to 6.752 for Ni, 0.037 to 1.875 for Pb, and 2.896 to 4.577 for Zn. The metal contents distribution in the residual portion was as follows: 1.28 to 5.70 for Pb, 17.70 to 40.0 for Zn, 10.66 to 28.70 for Cr, 7.93 to 17.82 for Cu, 11.40 to 35.30 for Ni, and 0.0 to 0.020 for Cd.

Table 2. Karadağ Soil Samples for Heavy Metals Distribution using BCR Sequential Extraction Scheme (µg/g dry weight mean ± St Dev*) n is fifteen.

	Exchangeable, acid-and water soluble (S1)		**Reducible (S2)**		**Oxidisable (S3)**		**Residual (S4)**		**Total Σ (S1 + S2 + S3 + S4)**	
Metal	**Average ±St Dev.**	**Rate (%)**	**Average ±St Dev.**	**Rate (%)**	**Average ±St Dev.**	**Rate (%)**	**Average ±St Dev.**	**Rate (%)**	**Average ±St Dev.**	**Rate (%)**
Cd	0.070±0.021	45.8	0.034±0.030	22.2	0.029±0.026	19.0	0.02±0.008	13.1	0.153**±0.02**	100
Cr	0.093±0.040	0.4	0.918±0.364	3.9	2.840±0.954	12.1	19.71±5.861	83.7	23.561**±9.28**	100
Cu	0.286±0.264	1.4	3.040±1.037	14.6	3.656±0.568	17.6	13.82±2.838	66.4	20.802**±5.93**	100
Ni	1.412±0.743	5.1	3.602±1.980	13.1	3.157±1.399	11.4	19.41±7.042	70.4	27.581**±8.40**	100
Pb	0.107±0.128	1.2	5.465±1.534	60.1	0.578±0.448	6.4	2.94±1.081	32.3	9.09**±2.46**	100
Zn	1.074±0.771	2.8	5.950±2.769	15.6	3.385±0.449	8.9	27.81±6.009	72.8	38.219**±12.33**	100

3.3. Evaluation of Heavy Metal Contamination Level

Due to its intricate structure, soil, which is a dynamic natural resource for human life, is a primary recipient of persistent pollutants, including heavy metals. All soils have natural concentrations of heavy metals called background. The quantity of the background of a metal depends on the mineral composition of the bedrock that developed the soil (Scazzola et al. 2003). Changes in heavy metal levels in soil vary according to the amount in the bedrock, enrichment, or leaching status. The individually total quantity of heavy metals in the soil is inadequate to accurately describe their efficacy and level of contamination. Therefore, when evaluating heavy metal pollution and learning how it affects living things, evaluating the impacts of many heavy metals as well as the effect of one heavy metal alone produces significantly superior findings. Numerous soil pollution quality indices suggested by different researchers have been successfully used in the evaluation of heavy metal pollution in soils. The heavy metal concentrations in various fractions of soils in this investigation as well as total heavy metal amounts were evaluated with the following heavy metal pollution indices and both the individual and cumulative impacts of metals on pollution were identified. These results led to the determination of the levels of heavy metal contamination in the soils of the research region that were developed on the volcanic material in the study area. The pollution indices showing the individual and cumulative effects of heavy metals in soil samples collected from the research region are shown in Table 3 and the categories and descriptions of the employed indices are provided in Table 4. The Enrichment Factor (EF) is a method used in the evaluation of metal pollution due to human-induced contamination and pollutants. The enrichment of an element is commonly defined as a rise in the concentration of that element along the soil profile from the source material to the surface. The following formula was used to obtain the enrichment factor, based on Hasan et al. (2013).

$$EF = (CX/C_{Fe})\ \text{soil}/(CX/C_{Fe})\ \text{referans}$$

Where,

(CX/C_{Fe}) soil: The metal content ratio investigated for the Fe content in the soil sample, (CX/C_{Fe}) referans the proportion between the Fe concentration and the metal concentration that was examined in the reference rock.

The reference rock metal concentration is the quantity of elements in the pertinent rock in the earth's crust (Taylor and McLennan 1985). The EF in Karadağ varied from 0.10-0.34 for Cd, 0.13-0.34 for Cr, 0.47-0.77 for Cu, 0.34-1.11 for Ni, 0.13-0.39 for Pb, and 0.27-0.54 for Zn, as seen in Table 3. These results suggest that there is no enrichment in the soils of Karadağ when the calculation is conducted using the contents of reference rocks. Except for two sample points, Ni's EF was always less than 1. The EF value is below 2 for these two sample locations and exhibits minimal enrichment.

Table 3. Pollution Index Values for the Research Area's Soils

Sample No	EF						Igeo						Multi Metal	
	Cd	Cr	Cu	Ni	Pb	Zn	Cd	Cr	Cu	Ni	Pb	Zn	PLI	Cd
1	0.24	0.20	0.72	0.52	0.23	0.54	-2.25	-2.52	-0.70	-1.15	-2.35	-1.11	0.47	3.17
2	0.16	0.13	0.47	0.34	0.17	0.30	-2.82	-3.22	-1.32	-1.79	-2.77	-1.96	0.30	2.01
3	0.12	0.14	0.60	0.44	0.16	0.29	-3.26	-3.04	-0.95	-1.40	-2.85	-1.98	0.32	2.27
4	0.23	0.13	0.62	0.41	0.13	0.27	-2.35	-3.21	-0.90	-1.52	-3.19	-2.12	0.32	2.29
5	0.22	0.25	0.77	0.68	0.25	0.39	-2.41	-2.23	-0.59	-0.78	-2.22	-1.58	0.48	3.29
6	0.10	0.22	0.66	0.58	0.24	0.38	-3.57	-2.38	-0.82	-0.99	-2.30	-1.62	0.39	2.81
7	0.34	0.33	0.64	1.11	0.25	0.47	-1.79	-1.80	-0.86	-0.07	-2.20	-1.32	0.59	4.05
8	0.24	0.34	0.73	0.82	0.39	0.52	-2.25	-1.76	-0.67	-0.51	-1.57	-1.18	0.60	3.93
9	0.14	0.20	0.54	0.50	0.27	0.43	-3.07	-2.52	-1.10	-1.21	-2.12	-1.42	0.40	2.69
10	0.20	0.27	0.63	0.54	0.19	0.40	-2.52	-2.12	-0.87	-1.11	-2.60	-1.54	0.43	2.88
11	0.25	0.24	0.62	0.59	0.19	0.36	-2.24	-2.29	-0.90	-0.99	-2.60	-1.70	0.43	2.89
12	0.23	0.29	0.58	1.09	0.19	0.39	-2.34	-1.98	-1.00	-0.10	-2.65	-1.56	0.49	3.57
13	0.14	0.29	0.66	0.70	0.19	0.41	-3.07	-2.02	-0.82	-0.73	-2.63	-1.49	0.43	3.08
14	0.16	0.25	0.54	0.51	0.17	0.31	-2.85	-2.24	-1.10	-1.19	-2.79	-1.92	0.37	2.49
15	0.25	0.21	0.72	0.47	0.21	0.35	-2.22	-2.50	-0.70	-1.30	-2.46	-1.71	0.43	2.85
Sample No	**Cf**						**RAC (%)**						**Multi Metal**	
	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Cd**	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**MCd**	**PI**
1	0.31	0.26	0.93	0.67	0.30	0.69	47.13	0.27	1.09	3.67	3.12	3.67	0.53	0.36
2	0.21	0.16	0.60	0.43	0.22	0.39	43.75	0.94	7.57	4.67	0.31	9.23	0.34	0.23
3	0.16	0.18	0.78	0.57	0.21	0.38	65.85	0.78	1.76	4.03	1.51	3.78	0.38	0.27
4	0.29	0.16	0.80	0.52	0.16	0.34	54.09	0.47	2.20	5.19	3.13	3.60	0.38	0.26
5	0.28	0.32	0.99	0.88	0.32	0.50	49.29	0.26	0.87	8.75	0.87	1.69	0.55	0.40
6	0.13	0.29	0.85	0.75	0.31	0.49	79.74	0.59	0.57	6.56	0.00	1.08	0.47	0.34
7	0.43	0.43	0.83	1.43	0.33	0.60	46.33	0.22	0.82	1.59	3.67	1.08	0.68	0.53
8	0.32	0.44	0.94	1.05	0.51	0.66	37.04	0.45	0.35	7.23	0.00	1.76	0.65	0.48
9	0.18	0.26	0.70	0.65	0.35	0.56	33.97	0.35	0.63	4.06	0.00	6.03	0.45	0.32
10	0.26	0.34	0.82	0.70	0.25	0.52	49.86	0.22	0.94	4.26	0.00	3.62	0.48	0.34
11	0.32	0.31	0.80	0.75	0.25	0.46	48.19	0.58	0.77	9.77	3.65	1.08	0.48	0.35
12	0.30	0.38	0.75	1.40	0.24	0.51	63.84	0.25	1.50	3.75	1.46	1.28	0.59	0.48
13	0.18	0.37	0.85	0.90	0.24	0.53	91.45	0.12	1.85	1.63	0.00	1.19	0.51	0.38
14	0.21	0.32	0.70	0.66	0.22	0.40	40.74	0.33	0.91	6.95	1.18	1.84	0.42	0.30
15	0.32	0.27	0.92	0.61	0.27	0.46	46.99	0.77	0.73	8.35	0.37	2.88	0.47	0.33

The Geoaccumulation Index, or Igeo, was created by Muller in 1969 and is used to determine the degree of pollution present in a sediment sample as well as to help identify and categorize it into different pollution classes. The Geoaccumulation Index, or Igeo, was created by Muller in 1969 and is used to determine the degree of pollution present in a sediment sample as well as to help identify and categorize it into different pollution classes.

$$\mathrm{Igeo} = \log 2\left(\frac{\mathrm{Cn}}{1.5\mathrm{xBn}}\right)$$

Where,

The measured concentration of the heavy metal in the soil sample is denoted by Cn, the background matrix correction factor resulting from lithogenic effects is 1.5, and Bn is the geochemical background (reference) value in the earth's crust average of n elements. For all metals in Karadağ (Igeo), the quantities less than 0 were found at all sample points, as demonstrated by the outcomes listed in Table 3. Considering these results, it was found that the Igeo assessment was uncontaminated. Although the terms contamination and pollution are often used interchangeably, it should be kept in mind that these terms do not mean exactly the same. Accordingly, the term "contamination refers" to the existence of an unnatural material at quantities that are higher than background levels. Pollution, on the other hand, is a contamination that causes or results in adverse biological effects. This difference makes it clear that pollution is a significant form of contamination.

Table 4. Categories and Qualification for the Used Indexes

EF	Qualification of Sediment	Igeo	Qualification of Sediment	PLI	Qualification of Sediment	RAC	Qualification of Sediment
<1	No Enrichment	≤ 0	Unpolluted	PLI< 0	Uncontaminated	<%1	No Risk For The Environment
<2	Minimal Enrichment	0<Igeo<1	Slightly Polluted	0 <PLI< 1	Uncontaminated to Moderately Contaminated	% 1-10	Low Risk
2-5	Moderate Enrichment	1<Igeo<2	Moderately Polluted	1 <PLI< 2	Moderately Contaminated	% 11-30	Moderately Risk
5-20	Considerable Degree of Enrichment	2<Igeo<3	From Moderately Polluted to Strongly Polluted	2 <PLI< 3	Moderately to Highly Contaminated	% 31-50	High Degree Risk
20-40	Very High Enrichment	3<Igeo<4	Strongly Polluted	3 <PLI< 4	Highly Contaminated	>%50	Very High Risk
>40	Extremely High Enrichment	4<Igeo<5	From Strongly Polluted to Extremely Polluted	4 <PLI< 5	Highly to Very Highly Contaminated	-	-
		5≤Igeo	Extremely Polluted	PLI>5	Very Highly Contaminated		
Cf	**Qualification of Sediment**	**Cd**	**Qualification of Sediment**	**mCd**	**Qualification of Sediment**	**PI**	**Qualification of Sediment**
Cf < 1	Low Contamination	Cd< 10	Low Degree of Pollution	mCd< 1	Nil to a Very Low Degree of Pollution	PI < 1	Unpolluted
1 < Cf <3	Moderate Contamination	10<Cd< 20	Moderate Degree of Pollution	1 <mCd< 3	Low Degree of Pollution	1 <PLI< 3	Low Degree of Pollution
3< Cf< 6	Considerable Contamination	20 <Cd< 40	Considerable Degree of Pollution	3 <mCd< 6	Considerable Degree of Pollution	3 <PLI< 5	Moderate Degree of Pollution
Cf > 6	Very High	Cd>40	High Degree of Pollution	mCd> 6	High Degree of Pollution	PLI >5	High Degree of Pollution

Pollution is not always the result of contamination; rather, pollution is the result of concentration levels that have detrimental impacts on organisms that might be deemed substantial. Pollution factor (Cf) is also an indicator widely used by many researchers to evaluate the anthropogenic effects of heavy metals in sediment samples and to reveal the extent of environmental pollution. "Average threshold values" or "mean crustal values" are used to calculate the pollution factor. Because of this, calculations were made of the soil pollution factors in the research region.

The ratio of the metal concentration at each sample location to the quantity of that metal in the earth's crust was used to create the equation below, which was used to find the pollution factor (Cf) (Hakanson, 1980). $\mathrm{Cf} = \mathrm{Cmetal}/\mathrm{Co}$

Where:

Cmetal: The amount of metal present in the soil sample; Co: The amount of metal present in the crust of the earth. The calculated Cf value was analyzed in 4 different pollution categories. According to Table 3 in Karadağ, Cf varied from 0.13 to 0.43 for Cd, 0.16 to 0.44 for Cr, 0.6 to 0.99 for Cu, 0.43 to 1.43 for Ni, 0.16 to 0.51 for Pb, and 0.34-0.69 for Zn. Even though there is a weak contamination at certain spots, it has been established that there is no pollution when all values are considered.

The term "RAC" refers to the acid and water soluble fraction (S1), which is used to assess the environmental dangers associated with heavy metals. (Li et al. 2013). The given formula below is used to compute RAC.

$$\mathrm{RAC}(\%) = \left(\frac{\mathrm{S1}}{\mathrm{S1} + \mathrm{S2} + \mathrm{S3} + \mathrm{S4}}\right) \mathrm{x}100$$

The increase in human activity is often what causes the water and acid soluble fraction (RAC). This fraction of heavy metals contains the more bioavailable and loosely bound portion (Jin et al., 2012). RAC in Karadağ; It varied between 33.97-91.45% for Cd, 0.12-0.94% for Cr, 0.35-7.57% for Cu, 1.59-9.77% for Ni, 0.00-3.67% for

Pb, and 1.08-9.23% for Zn. Although there is no pollution in the current situation, the pollution potential of these metals, especially Cd, goes from intermediate to high risky. Therefore, at higher rates of anthropogenic contamination, care should be taken as these metals have a high risk of mixing with groundwater and polluting plants and other living things. In the evaluations using other indices, there was no significant pollution or contamination in the soils, but RAC values were found to indicate a high risk, particularly for Cd. Although there is currently no high risk, sample points in the low risk group for Ni and Pb were found in the RAC evaluation. When the other soluble components are taken into account, notably for Cd and Pb the risk class increases even more especially for Cd and Pb. This circumstance demonstrates unequivocally that in pollution evaluations, indexes that take mobile fractions into account rather than total values should be used for sensitive areas.

The pollutant load index (PLI) was developed to compare the pollution status of different locations, to determine the extent of pollution and variation across different sampling stations. It can be defined as an integrated index since it collects all the heavy metals studied in a single index. Since all the metals under consideration are handled in a single index, they are frequently used to compare the pollution levels in various places. Each metal's pollution factors (Cf) are determined to produce the index. The pollutant load index (PLI) was created using the following formula (Tomlinson et al. 1980).

$$PLI= (Cf1 * Cf2 * Cf3 * \ldots.. * Cfn)1/n$$

$$Cf= Cmetal / Co$$

Where:

Cmetal: The amount of metal in the sediment sample
Co: The metal's fundamental (background) value
Cf: Pollution coefficient, n: Metal count

The PLI in Karadağ ranged from 0.30 to 0.60, with an average of 0.43, as shown in Table 3. The PLI ranges from 0 to 1, and there is no discernible contamination or pollution at any of the sample locations.

Hakanson (1980) recommended utilizing a diagnostic measure termed the degree of contamination (Cd) to streamline contamination control. The total of all the pollution elements within a certain basin is its Pollution Degree (Cd). Cd has been calculated by adding up Cf for every sample.

$$\mathrm{Cd} = \sum_{i=1}^{i=n} \mathrm{Cf}$$

When the study area soils are evaluated in terms of Cd, all values in Karadağ are less than 10 and do not indicate any pollution (Table 3). The modified degree of contamination (mCd) approach may also be used to approximation the precise level of contamination.

For this objective, the following equation was used to obtain the modified contamination degree (mCd) (Abrahim and Parker, 2008).

$$\mathrm{mCd} = \frac{\sum_{i=1}^{i=n} \mathrm{Cf}}{n}$$

The mCd values of the soils and their reference ranges are presented in Table 3 and Table 4. The average mCd value in Karadağ varied from 0.34 to 0.68, with an average of 0.49. The results obtained at all points in Montenegro are less than 1 and do not indicate any pollution in terms of the total effect of metal pollution.

Pollution indexes (PI) of heavy metals in soils were also determined using the soil environmental quality standards of Canadian soil quality guidelines for the protection of the environment and human health. PI was calculated using the following formula.

$$\mathrm{PI} = \mathrm{Ci}/\mathrm{Si}$$

PI values varied between 0.23-0.53 in Karadağ. PI values calculated for each element, taking into account the maximum allowable metal content for human health, showed that there was no pollution that would pose any health risk.

4. Conclusions

The contents of Cd, Cr, Cu, Ni, Pb, and Zn in mobile and residual fractions of soils obtained from Karadağ volcanic rocks were evaluated in this work using the BCR sequential extraction procedure, and the mobility of each metal was revealed based on fractions. The levels of heavy metal contamination and pollution in the area, both in terms of individual and cumulative impacts, have also been determined using several pollution indices and additionally to the concentrations of heavy metals in the area's mobile and immobile fractions. None of the used indices, with the exception of RAC, indicated any pollution in the soils investigated. It was determined that these levels obtained did not cause any pollution in the soil. While assessments using other indices revealed no appreciable pollution or contamination in the soils, RAC values indicated a high risk, particularly for Cd. Some sample spots for Ni and Pb were found in the low-risk group, although not being high risk. According to RAC values although not high-risk for Ni and Pb some sampling spots were found in the low-risk group. With the help of this study, it was found that the BCR sequential extraction process may offer useful data for a range of management and organization applications (fertilization, spraying, etc.) in agricultural fields. It has been shown that using sequential extraction methods and various pollution indicators, the metal availability across different soil components, the possible impacts on the environment, and the risk of contamination may all be assessed more efficiently. The finding shows that assessments using pollution indices can serve to design and undertake effective strategies and measures to prevent further degradation of the soil environment in future farmland and regions with prospective pollution issues.

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