Original Research

Risk Assessment and Chemical Fractionation of Heavy Metals by BCR Sequential Extraction in Soil of the Sapanca Lake Basin, Turkey

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Abstract

Sapanca Lake is an important drinking water source located by D-100 highway in the north and E-80 (TEM Anatolian Highway) and a railway line in the south. Heavy metal concentrations in roadside soils result from vehicle exhausts and the corroding metal parts of vehicles. Due to the difficulty of removing heavy metals from the soil, a significant pollution problem arises and this pollution also affects the water resources by means of rain. Although there are several industries, the highway located near the lake is the most important pollutant source for Sapanca Basin. Therefore, this study evaluated heavy metal concentrations, the chemical fractions of the metals and ecological risks (by using C_f, RAC and PERI) in the soil samples collected seasonally between 2015 and 2017 in Sapanca Lake Basin. Al and Fe were determined at very high amounts in all stations and the relationship between mean concentrations of other metals was determined to be Zn>Ba>As>Ni>Cr>Pb>Cu>Co>Cd. However, Zn, Ba, As, Ni, Cr, Pb, Cu, Co and Cd mean concentrations were determined as 87.63 mg/kg, Ba 86.87 mg/kg, 80.40 mg/kg, 58.62 mg/kg, 50.42 mg/kg, 41.90 mg/kg, 38.16 mg/kg, 13.98 mg/kg, 2.89 mg/kg respectively. Al, Fe, Co, Cr, Cu, Ni and Zn are mainly found in residual fractions in soil. According to the environmental risk assessment on the basis of soil stations, the 7th station has the highest GC_f value, which means that the soil sample presents the highest environmental risk according to the contamination factors. On the other hand, Cd has serious potential ecological risk and As has considerable potential ecological risk in all stations.

Keywords: heavy metal, ecological risk, Sapanca Lake, soil pollution, sequential extraction

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Introduction

Heavy metal pollution is at the top of the list of causes and other chemical pollutants that can arise from various sources, being resistant to environmental conditions, and can easily enter the food chain and accumulate in increasing concentrations in living organisms [1, 2]. Heavy metals have high environmental durability, and heavy metal can enter soil through natural sources and anthropogenic sources such as: weathering of rocks, precipitation, traffic, industry and agricultural activities [3]. Heavy metals, which are trace elements, are identified as metal or metalloids, having a specific density greater than 5 gr/cm³ [4]. Long-term accumulation of heavy metals in the soil threatens human health through the food chain and ecosystem. So, heavy metals have become the most important pollutants in soil all over the world [5].

Soil pollution is a major environmental issue worldwide and has an important role for many different pollutants and particularly, the largest receiving environment exposed to all metal pollution in the ecosystem [1]. Heavy metal accumulation can reduce the quality of agricultural products, reduce product yield, impair soil quality and directly affect the physicochemical properties of soil. Contrary to the majority of organic pollutants that have lost toxicity due to biodegradation, they can cause long-term toxic effects since metals are not degraded [6, 7]. Also, depending on the physicochemical characteristics of the soil, such as ORP, pH, conductivity, soil texture, organic matter and organic carbon, heavy metals may enter from the soil to the aquatic ecosystem and contaminate the drinking water system [8, 9]. Heavy metal pollution in soil has become an important problem worldwide and researchers have focused on this pollution [10-13].

Heavy metals accumulate in different geochemical fractions (organic-associated, exchangable, carbonate-associated, Fe, Mn oxide-associated and phyllosilicate minerals) in soils or sediments. In the soil or sediment, the bioavailable concentrations of trace elements are analyzed by using sequential extraction procedures that are commonly used to examine the mobility of trace elements in the soil [11, 14-17]. In the soil analyzed by this method; information on total concentrations, mobility and toxicity of heavy metals can be obtained. For this purpose, a standard consecutive extraction method has been prepared and used by the European Union Reference Commission (BCR – the European Community Bureau of Reference) in order to compare the results determined by different consecutive extraction methods in a healthy way [1, 18]. In the BCR method, whose new name is SM & T (The Standard Measurement and Testing Program), heavy metal fractions are listed as follows: can be changed and evaluated in three steps depending on carbonates, reducible (depending on Fe- and Mn-oxides), and oxidizable (depending on organic matter and sulfides).

As the fourth step, the residual part contains metals bound to soluble minerals in strong acid mixtures.

This extraction method has been used to estimate the fractionation and total concentration of heavy metals in soils in numerous studies. For example, in the study by Zemberyova et al. (2006), the modified BCR sequential extraction method was used for heavy metal determination in different Slovakian soils. Cd, Cr, Cu, Ni, Pb and Zn results have been reported to be satisfactory for the study [19]. Nannoni et al. (2011) studied the fractions of As, Cd, Cu, Pb, Sb and Zn in northern Kosova mining areas. It has been reported that the pollutant levels are high in general and local areas, while the values of Pb, Zn, Cd and Sb increase as the mining areas are approached. It has been reported that lead is generally present in the mobile fraction (the sum of the first three digits of the BCR method), the Cd element is more extrudable and reducible, and the As, Cu, Sb and Zn elements are in the residual fraction. The order of mobility of heavy metals is reported as Cd>Zn>Pb>Sb>As>Cu [20].

On the other hand, the ecological risks of heavy metals in soil can be examined using many different pollutant indexes [5, 9, 21-25]. In these studies, the ecological risks of heavy metals were assessed by total concentration of the metals in soil or sediment. Total concentration of the metals can't provide effective ecological risk assessment in soil or sediment [8, 11, 25, 26]. So, heavy metal concentrations in soil should be determined according to the metal fractions. Determining concentrations by fractionation into fractions of heavy metals allows for a more detailed interpretation of possible sources of contaminants of heavy metals and a more reliable risk assessment.

Sapanca Lake is an important drinking water source located alongside the D-100 highway in the north and alongside E-80 (TEM Anatolian Highway) and a railway line in the south. Heavy metal concentrations in roadside soils result from vehicle exhausts and the corroding metal parts of vehicles. Due to the difficulty of removing heavy metals from the soil, a significant pollution problem arises and this pollution also affects the water resources by means of rain. Although there are several industries, the highway located near the lake is the most important pollutant source for Sapanca Basin. The aim of this study is to detect heavy metal pollution in the basins of Lake Sapanca in Turkey – an important source of drinking water. It also examines the degree of heavy metal pollution in the soil by ecological risk assessment using different methods.

Material and Methods

Study Area and Sampling Strategy

Sapanca Lake is a freshwater lake located in the Marmara region at a height of 30 m above sea level

Fig. 1. Map of soil samples in Sapanca Lake basin.

in a tectonic pit. It extends parallel to Iznik Lake and reaches up to Adapazari Plain as a continuation of Izmit Bay (Fig. 1). It is known that underground waters also feed the lake. Fruit, vegetable and cereal production are important agricultural activities to the south and southwest of the lake. The use of pesticides and chemical fertilizers is widespread in the region in order to protect agricultural products against disease and harm, and to increase productivity. Sapanca Lake is used both as a drinking water source and as process water for factories and facilities. The D-100 highway is located in the north of the lake, TEM Anatolian Highway and railway are located in the south. As a result of this heavy traffic, there are gas stations on the coast of the lake [27].

70 soil samples were taken from 0-40 cm depth from 10 points around the lake to represent the Sapanca Basin in Fig. 1. Samples were collected from soils according to the TS (Turkish Standards Institute) Standard "Soil Quality-Surface Soil Sampling, Sampling and Storage Rules of Samples" numbered 9923 and dated March 1992. Soil samples were taken with a removable soil tube sampler, transferred to plastic bags and then brought to the laboratory in safety.

Analysis Methods

Firstly, the glass and laboratory materials were washed with detergent and rinsed and then allowed to stand overnight in a 10% HNO_3 solution. The materials were removed from the acid solution and passed through deionized water and then dried at 105ºC. The soil samples were dried at 105ºC until hard weighing was obtained, and samples were ground in porcelain mortar and then sieved with 100 mesh and 230 mesh

sieves. Organic matter, organic carbon, conductivity, pH, oxidation-reduction potential (ORP), and salinity parameters were determined according to standard methods.

The soil was measured with a YSI Professional Plus Multiparameter in suspension (pH), salinity, conductivity, oxidation-reduction potential (ORP), and 1:5 (soil:water ratio) suspension. 5 grams of soil sample was weighed, 25 mL of purified water was added, and a shaker was mixed for 1 hour. Measurements were made on the liquid part, which was clear on the top of the suspension.

BCR Sequential Extraction Method

After collecting the soil samples, heavy metal concentrations were identified in accordance with the methodology presented by Tessier et al. (1979) and the four-step successive extraction method (current name) (BCR – the European Community Bureau of Reference) developed by the commission, which is the European Standards, Measurements and Testing Program of the European Commission [28]. The four-step BCR sequential extraction procedure is summarized below.

1g soil samples were placed into 50 mL PE tubes and then the procedure was applied as shown in Table 1. After each fraction process, the supernatant liquid was decanted into a 50 mL PE tube and stored at 4ºC prior to analysis. Only the supernatant liquid in the residual fraction was completed to 50 mL with nitric acid and stored at 4ºC. The determinations of levels of Al, As, Ba, Cd, Co, Cr, Cu, Fe, Ni, Pb and Zn in the extracts were performed by ICP-OES.

Table 1. BCR sequential extraction procedure.

Fractions	Fraction in Soil	Extract material	Shaking time and temperature
F_1	Exchangeable metals	40 mL 0.11 M CH_3COOH	200 rpm and16 hour at laboratory temperature
F_2	Metals bound to iron and manganese oxides (reducible)	40 mL 0.5 M $HONH_2.HCl$ (pH 1,5)	200 rpm and16 hour at laboratory temperature
F_3	Metals bound to organic matter and sulfides (oxidizable)	10 mL 8.8 M H_2O_2 (pH 2) , 10 mL 8.8 M H_2O_2 (pH 2) 50 mL 1 M NH_4OAc (pH 2)	200 rpm and 1 hour at laboratory temperature 1 hour at 85ºC (is only heated) 1 hour at laboratory temperature
F_4 (R)	Residual	15 mL aqua regia	It is heated to the dryness and constant volume is completed

However, the reagents and chemicals were all at analytical grade. Reagent blanks, calibration with standard solutions, triplicate samples and the standard reference materials (BCR-701) were performed to guarantee quality assurance and quality control. The recovery ratios were determined as over 95% for each heavy metal (Cd 98%, Cr 95%, Cu 95%, Ni 97%, Pb 99%, Zn 101%).

Results and Discussion

Soil Properties

Physicochemical characteristics of soil affect heavy metal accumulation and mobility of the metals in the soil. Depending on ORP, pH, conductivity, soil texture and organic matter, heavy metals can be transferred from the soil to the aquatic system and contaminate the water sources. Especially pH, ORP and organic matter play an important role in the mobility of heavy metals in soils or sediments. As has been presented in Table 2, pH and conductivity values range from 6.49 to 8.63, and 150.10 µS/cm to 625.40 µS/cm. Organic matter content of Sapanca Lake basin is very low. The rate of maximum organic matter is 14.39% and the rate of maximum organic carbon is 8.35%. Soils primarily consist of sand and silt in all stations (except the 4th and 7th stations), as shown in Fig. 2. The highest silt (52%) content is determined in the 8th station and the highest sand content is 65% in the 9th station and 61% in the

2nd station, respectively. Soil samples have gravel texture except the 8th and 9th stations. Most anthropogenic contaminants are associated with the clay and silt fractions [29]. Generally, the silt content has a high percentage in all soil samples in Sapanca Lake basin.

On the other hand, soils rich in clay and organic matter hold heavy metals and form tough soluble compounds. Keeping heavy metals in the soil varies depending on the amount of organic matter in the soil and the type of clay minerals. Movement of heavy metals into the mobile is of great importance for both plants and bottom waters. Heavy metals that accumulate in soils can be washed from the soil depending on the pH value in shallow, coarse (sandy) and organic matter content in low soils and mixed with groundwater.
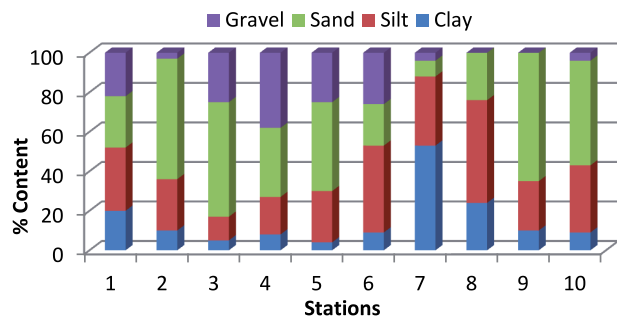

Fig. 2. Soil face distributions in Sapanca Lake.

Table 2. Basic statistics of physico-chemical parameters.

	C (µS/cm)	SAL (ppt)	pH	ORP (mV)	OM %	OC %
Min	150.10	0.01	6.49	111.40	1.94	1.12
Max	625.40	0.34	8.63	352.50	14.39	8.35
Median	284	0.14	7.91	243.40	6.15	3.57
Mean	302.17	0.13	7.87	245.24	6.50	3.77
Std	109.60	0.07	0.45	49.38	2.81	1.63

C: conductivity, Sal: salinity, ORP: oxidation-reduction potential, OM: organic matter, OC: organic carbon

Table 3. Total heavy metals concentrations (mg/kg).

Stations	HM										
	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn
1	112715.35	84.88	119.29	3.05	13.89	55.22	32.22	379892.90	70.76	37.22	68.53
2	16211.32	78.57	93.94	2.68	14.26	42.49	32.11	37230.19	64.14	36.21	69.29
3	13238.32	77.35	40.20	2.47	13.93	44.57	38.57	37632.45	63.87	39.07	79.14
4	12355.89	81.01	48.32	2.61	10.65	35.62	34.99	32308.68	43.85	37.21	70.45
5	11163.81	76.04	61.25	2.48	10.74	45.36	42.33	30323.50	46.96	47.30	147.77
6	16190.98	73.75	46.68	2.64	11.70	62.45	34.46	35518.95	52.60	44.49	84.65
7	26100.26	79.96	125.88	3.63	23.66	50.76	41.74	44639.03	57.85	60.85	74.45
8	19303.12	81.85	121.91	2.76	12.88	60.61	39.55	36213.80	63.08	35.28	87.01
9	19121.90	84.49	98.11	3.01	14.04	54.28	44.57	36402.71	57.12	40.46	102.58
10	15252.07	83.19	117.31	3.17	13.02	47.06	38.59	31732.82	61.72	38.67	92.46
Min	11163.81	73.75	40.20	2.47	10.65	35.62	32.11	30323.50	43.85	35.28	68.53
Max	112715.35	84.88	125.88	3.63	23.66	62.45	44.57	379892.90	70.76	60.85	147.77
Mean	26165.30	80.11	87.29	2.85	13.88	49.84	37.91	70189.50	58.20	41.68	87.63

Heavy Metal Levels in Soil

The statistical heavy metal results of samples are presented in Table 3. Soil samples were digested by using the aforementioned BCR sequential extraction method, and heavy metal concentrations were determined in ICP-OES. As presented in Table 3, total heavy metal concentrations can be given on the basis of the stations and the concentrations of Al and Fe are far greater than the other metals. Consequently, the soil of Sapanca Lake basin is very rich in these two elements, which originated from crustal [30]. The heavy metal concentrations are Fe>Al>Zn>Ba>As>Ni>Cr>Pb>Cu>Co>Cd. The total heavy metal concentrations are determined as: As 73.75-84.88 mg/kg, Ba 46.20-125.88 mg/kg, Cd 2.47-3.63 mg/kg, Co 10.65-23.66 mg/kg, Cr 35.62-62.45 mg/kg, Cu 32.11-44.57 mg/kg, Ni 43.85- 70.76 mg/kg, Pb 35.28- 60.85 mg/kg and Zn 68.53-147.77 mg/kg. The maximum values of heavy metal were observed at the 7th station, which is located near agricultural and industrial areas. However, the maximum values of As and Ni are determined at the 1st station while Cr, Cu and Zn values are determined at the 6th, 9th and 5th stations, respectively.

Fig. 3 shows a histogram of heavy metals in Sapanca Lake basin. The results show that Al and Fe are dominantly found in the residual fraction and these elements, which originated from earth's crust, are not associated with the exchangeable fraction in the soil samples. The dominant fraction of Cr, Ni and Zn is the residual fraction, which accounts for 81.5%, 61.36% and 53.45% of the total concentration, respectively. It is likely that the heavy metals associated with the residual fractions are involved in the aluminosilicate minerals and so are unlikely to be released into pore-waters through dissociation [3].

The distribution pattern of Co is as follows: exchangeable fraction (11.19%) < oxidizable fraction (14.29%) < reducible fraction (32.99%) < residual fraction (41.51%). So, the residual fraction is the main fraction for Co. A noticeable amount of Cd is observed in the residual fraction (37.94%) and the other fractions decrease in the order as follows: reducible fraction (22.77%) > oxidizable fraction 21.86% > residual fraction 17.41%. The levels of Cu in soils are mainly found in the residual fraction and the percentage of the fractions are as follows: 37.94% residual, 27.55% reducible, 15.62% oxidizable and 7.13% exchangeable fraction. As, Ba and Pb are distributed in all fractions of the soil, but the dominant fractions are determined in the oxidizable (33.52% for As) and reducible fraction (44.72% and 39.36% for Ba and Pb).

Generally, heavy metals are mainly observed in the residual fraction at all stations (as shown in Fig. 3). Al and Fe elements are dominantly found in the oxidizable fraction (43.13% and 46.33%) in the 1st station, and Cr and Ni are mostly observed in the oxidizable fraction (21.96% and 24.16%) in the 7th station. For Co, the main fraction is the reducible fraction in the 7th station.

Correlation Analysis for Heavy Metals and Physicochemical Characteristics

Table 4 shows the relationship between heavy metals in the soil of Sapanca Lake basin. A significant and positive correlation is observed between Al and Fe ($r^2 = 0.996$), As and Cd ($r^2 = 0.925$) and Ni and Cr
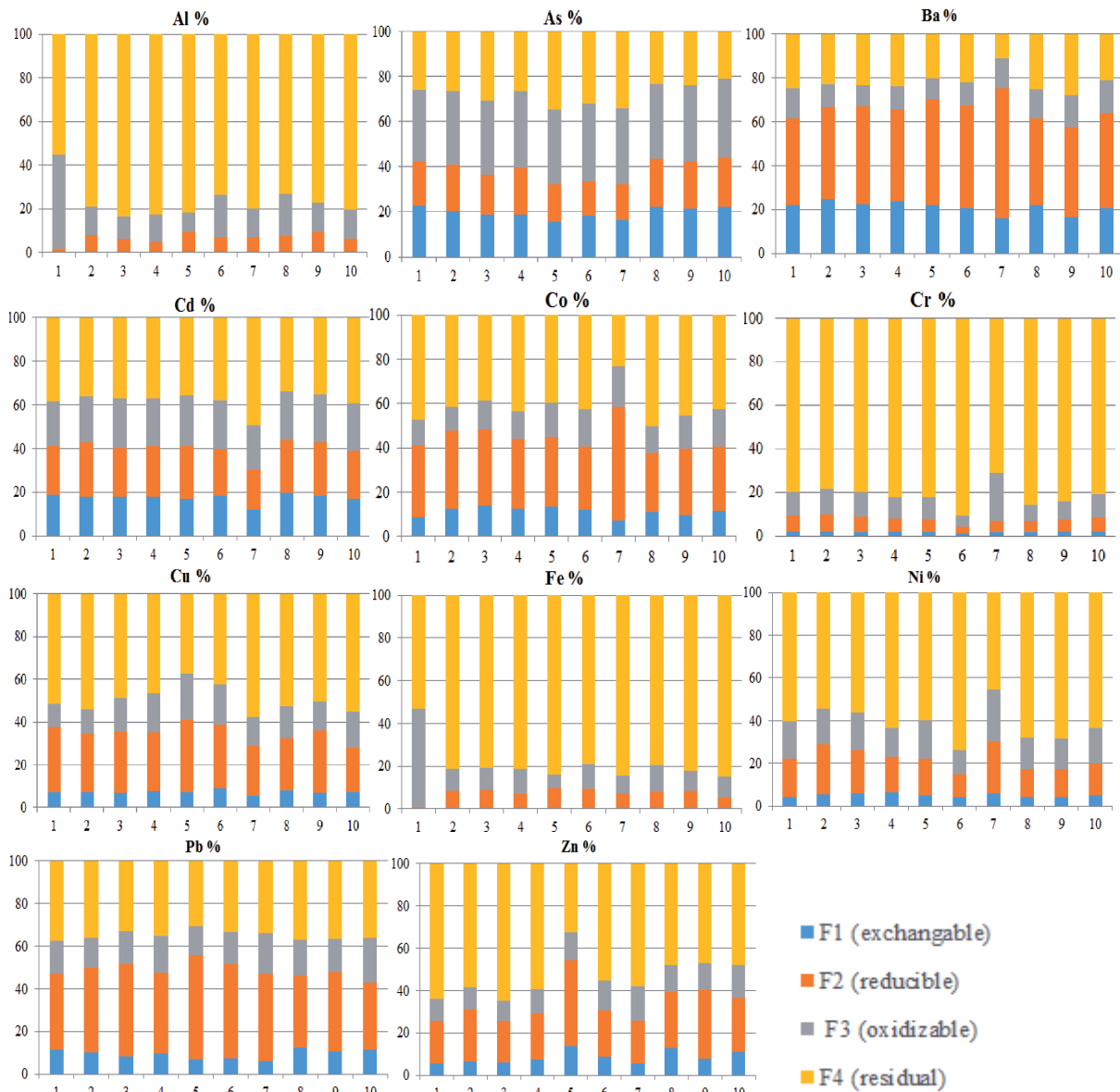
Fig. 3. Fractionation distribution characteristics of trace elements.

(r^2 = 0.903) (Table 4). This state means that these heavy metals may have originated from the same pollutant source and that these metals have some similar properties. There is no correlation between Ba and the other metals, which indicates that Ba can originate from various pollutant sources. The correlations (in which r^2 between these metals is higher than 0.50) among Cd, Co, Cu and Pb are significant. A positive correlation is observed between As and Co, Cr, Cu, Ni and Pb. On the other hand, a positive correlation between pH, ORP and SAL is observed. There is a positive correlation among ORP, pH, As and Cd, and Cr – ORP correlation is significant.

Evaluating Soil Heavy Metal Pollution

In order to evaluate heavy metal pollution in Sapanca Lake Basin, we performed three pollution indexes: the contamination factors (C_f) of metals, risk assessment code (RAC) and potential ecological risk index method (PERI).

Contamination Factor (C_f)

The calculation of contamination factor of heavy metals is an important parameter that identifies the degree of risk of heavy metals to the environment in relation to its retention time [3]. The individual contamination factor (C_f) for the 11 metals was calculated according to Fernandes (1997) [31]. C_f is calculated by dividing the sum of heavy metal concentrations in the mobile fraction (exchangeable, acid-reducible and oxidizable-organic forms) by the residual fraction [3]. The global contamination factor (GC_f) was determined as the sum of the C_f values [32].

Table 4. Pearson correlation of heavy metals and physicochemical characteristics.

	C	SAL	pH	ORP	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn	OM	OC
C	1																
SAL	,265*	1															
pH	,095	,537**	1														
ORP	-,251*	-,848**	-,560**	1													
Al	,010	-,058	-,090	,026	1												
As	,210	,617**	,554**	-,704**	-,088	1											
Ba	-,092	,001	,017	,093	,192	,127	1										
Cd	,181	,641**	,660**	-,697**	-,097	,925**	,106	1									
Co	,150	,355**	,308**	-,339**	-,043	,566**	,353**	,652**	1								
Cr	,131	,495**	,363**	-,506**	-,062	,533**	,132	,533**	,468**	1							
Cu	,107	,099	,119	-,183	-,131	,432**	,061	,524**	,437**	,227	1						
Fe	-,007	-,044	-,060	,009	,996**	-,059	,172	-,068	-,050	-,043	-,117	1					
Ni	,062	,388**	,294*	-,398**	-,014	,533**	,249*	,503**	,587**	,903**	,219	,005	1				
Pb	,235*	,287*	,208	-,350**	-,132	,522**	,013	,655**	,687**	,347**	,636**	-,129	,296*	1			
Zn	-,007	-,021	-,078	-,056	-,082	,116	-,043	,161	,002	,050	,704**	-,066	-,017	,415**	1		
OM	,076	,036	-,166	,128	-,150	-,074	,319**	,006	,362**	,127	,285*	-,177	,087	,424**	,183	1	
OC	,076	,036	-,165	,127	-,150	-,074	,319**	,007	,363**	,127	,285*	-,177	,087	,424**	,182	1,000**	1

C: Conductivity Sal: Salinity ORP:oxidation-reduction potential OM: organic matter OC: organic carbon

*Correlation is significant at the 0.05 level. ** Correlation is significant at the 0.01 level.

Table 5. Contamination factor values of heavy metals in soil.

Stations	C_f											GC_f
	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn	
1	0.81	2.82	3.02	1.59	1.11	0.25	0.94	0.89	0.66	1.67	0.57	14.33
2	0.26	2.77	3.37	1.78	1.40	0.28	0.85	0.23	0.84	1.77	0.71	14.25
3	0.20	2.26	3.30	1.69	1.59	0.26	1.05	0.24	0.77	2.03	0.54	13.93
4	0.21	2.78	3.23	1.71	1.29	0.21	1.15	0.23	0.58	1.85	0.68	13.90
5	0.23	1.87	3.98	1.79	1.53	0.21	1.65	0.19	0.67	2.27	2.09	16.49
6	0.35	2.14	3.57	1.65	1.34	0.10	1.37	0.27	0.36	1.99	0.81	13.95
7	0.25	1.92	8.12	1.04	3.35	0.40	0.74	0.18	1.20	1.96	0.73	19.89
8	0.36	3.25	2.96	1.97	0.98	0.17	0.90	0.26	0.48	1.69	1.09	14.11
9	0.29	3.23	2.56	1.85	1.19	0.19	0.98	0.22	0.46	1.74	1.13	13.85
10	0.24	3.77	3.80	1.55	1.34	0.24	0.82	0.18	0.57	1.75	1.09	15.35
Min	0.20	1.87	2.56	1.04	0.98	0.10	0.74	0.18	0.36	1.67	0.54	13.85
Max	0.81	3.77	8.12	1.97	3.35	0.40	1.65	0.89	1.20	2.27	2.09	19.89
Mean	0.32	2.68	3.79	1.66	1.51	0.23	1.04	0.29	0.66	1.87	0.94	15.01

Table 5 shows the calculated individual and global contamination factors of heavy metals in the soil samples at all stations. The 7th station has the highest GC_f value, which means that this soil sample carries the highest environmental risk. The GC_f values are identified as 7>5>10>1>2>8>6>3>4>9. Cr has the lowest C_f values, ranging from 0.10 to 0.40, and also Al, Fe, Ni and Zn values ranging from 0.20 to 0.81, 0.18 to 0.89, 0.36 to 2.09 and 0.54 to 2.09, respectively. Ba has the highest C_f values, ranging from 2.56 to 8.12, which mean that Ba can be removed from Sapanca Lake Basin at a faster rate than the other metals because a higher relative metal retention depending on the lower C_f values has been observed [32]. According to C_f, the As, Cd, Co, Cu and Pb are released from the 10th, 8th, 7th and 5th stations in Sapanca Lake basin, respectively. Generally, the chemical forms of these metals, except for Ba, are all dominated by the residual fractions in this study. On the other hand, the non-residual fraction is more suitable for the investigation of soil-plant systems and this fraction is an important factor that affects the mobility of heavy metals.

Risk Assessment Code (RAC)

In this method, pollution is calculated by dividing the metal of an exchangeable fraction (step 1) to the total content of the metal in all fractions. RAC is commonly used to examine the availability of the heavy metals in the eco-systems, and the method has an important role as an indicator of environmental health [12, 33]. The interpretation of RAC assessment is 'no risk' (RAC<1), 'low risk' (1~10%), 'medium risk' (11~30%), 'high risk' (31~50%) and 'very high risk' RAC≤75%)

[34]. Heavy metals are bound with different strengths to the fractions in the soils or sediments [27]. The calculation of risk assessment code depends on heavy metals, which are weakly bound to the solid fraction. So, the heavy metals cause a major environmental issue to the aquatic system due to bioavailability and toxicity [3]. RAC values of soil samples are presented in Table 6.

As presented in Table 6, the soils have a low risk for Cr, Cu and Ni, which has RAC values of less than 10%, which means that these metals have no remarkable mobility in Sapanca Lake basin. As, Ba and Cd indicate a medium risk in terms of the availability of the heavy metals in the environment. Co, Pb and Zn mostly indicate a medium risk and this issue can turn into a medium risk at all stations in the near future.

Potential Ecological Risk Index (PERI)

This method exhaustively regards the potential risk of heavy metals in soil or sediment [9, 35]. PERI was designed to assess the heavy metal content toxicity of trace elements in soil or sediment, the kind of pollutant and the toxicity level of heavy metal pollution. The method can be used for the assessment of soil in different areas and has been mostly preferred for environmental risk assessment [22, 36, 38]. The index is calculated as follows:

$$RI = \sum_{i=1}^{m} E_r^i = \sum_{i=1}^{m} T_r^i \frac{C_s^i}{C_n^i} \qquad (1)$$

$$E_r^i = T_r^i C_f^i \qquad (2)$$

Table 6. RAC values of heavy metals in Sapanca Lake Basin.

Stations	RAC %								
	As	Ba	Cd	Co	Cr	Cu	Ni	Pb	Zn
1	22.55	21.75	18.67	8.43	1.83	6.97	4.05	11.29	5.36
2	20.29	24.73	18.04	12.43	1.94	6.99	5.60	10.10	6.23
3	18.62	22.61	17.68	14.15	1.74	6.85	5.84	8.09	5.99
4	18.86	23.60	17.70	12.43	2.16	7.71	6.33	9.80	7.51
5	15.63	22.08	16.89	13.44	1.52	7.10	4.83	6.74	13.70
6	18.10	20.76	18.08	11.75	1.13	8.71	4.12	7.36	8.52
7	16.39	15.83	11.90	7.33	1.48	5.42	6.03	6.19	5.65
8	22.43	22.08	19.69	11.10	1.62	7.94	4.22	12.18	12.98
9	21.40	16.29	18.37	9.34	1.84	6.50	3.95	10.55	7.61
10	22.18	20.74	17.12	11.54	2.11	7.13	4.79	11.46	10.92
Min	15.63	15.83	11.90	7.33	1.13	5.42	3.95	6.19	5.36

The RI is the potential ecological risk index for multi metals, E_r^i is the PERI for a single heavy metal, C_f^i is pollution coefficient of the metal, and C_s^i and C_n^i are the measured and the background values of the metal. Background values were taken from Turekian and Wedepohl (1961) [37]. T_r^i is the toxic factor of the metal provided by Hakanson (1980) and these values are 10 (As), 30 (Cd), 2 (Cr), 5 (Cu, Ni, Pb) and 1 (Zn), respectively [35]. T_r^i reflects the toxicity level and ecological sensitivity to heavy metal pollution [38].

E_r^i and RI can be interpreted as: low ($E_r^i<40$), moderate ($40\leq E_r^i < 80$), considerable ($80\leq E_r^i<160$), high ($160\leq E_r^i<320$) and serious ($320\leq E_r^i$), and low (RI<150), moderate ($150\leq RI<300$), severe ($300\leq RI<600$) and serious ($600\leq RI$).

According to the potential ecological risk index calculation, the results of the heavy metals in the soil are presented in Table 7. The metals with E_r from the highest to the lowest level are Cd>>As>Pb>Ni>Cu>Zn>Cr. The potential ecological risk index of Cr, Cu, Ni, Pb and Zn in 10 stations are lower than 40, which means a low potential risk in Sapanca Lake basin. In addition, Cd is the main ecological risk factor, ranging from 370.61 to 545.11, because E_r values of Cd are far greater than Cr, Cu, Ni, Pb and Zn. As is the second dominant ecological risk factor, ranging from 122.91 to 141.46. Cd has

Table 7. Potential ecological risk of heavy metals in Sapanca Lake basin.

Stations	E_r							RI
	As	Cd	Cr	Cu	Ni	Pb	Zn	
1	141.46	456.83	1.10	2.93	4.72	14.89	0.98	622.91
2	130.95	401.30	0.85	2.92	4.28	14.48	0,99	555.76
3	128.92	370.61	0.89	3.51	4.26	15.63	1.13	524.94
4	135.01	391.70	0.71	3.18	2.92	14.88	1.01	549.42
5	126.73	371.37	0.91	3.85	3.13	18.92	2.11	527.02
6	122.91	396.58	1.25	3.13	3.51	17.80	1.21	546.39
7	133.27	545.11	1.02	3.79	3.86	24.34	1.06	712.45
8	136.42	413.70	1.21	3.60	4.21	14.11	1.24	574.49
9	140.81	450.85	1.09	4.05	3.81	16.19	1.47	618.26
10	138.65	476.16	0.94	3.51	4.11	15.47	1.32	640.16
Min	122.91	370.61	0.71	2.92	2.92	14.11	0.98	524.94
Max	141.46	545.11	1.25	4.05	4.72	24.34	2.11	712.45
Mean	133.52	427.42	1.00	3.45	3.88	16.67	1.25	587.18

serious potential ecological risk and As has considerable potential ecological risk in all stations. So, precautions should be taken against As and especially Cd in the soil and the effective pollution control for these metals should be implemented immediately.

Conclusions

Sapanca Lake is one of the most important sources of drinking water for the Marmara Region. Today, increasing environmental pollution and the threat of global warming have led to an increase in the number of studies on the protection and improvement of drinking water resources. Many factors affect drinking water resources. One of them is the structure and content of the basin soil. Drinking water resources in Turkey are examined at certain intervals and quality evaluation is carried out. However, it is not enough to protect the water resources. The aim of this study is to determine the heavy metal pollution in Sapanca Lake Basin and evaluate the ecological risks. At this point, improvements to the pollutants that will affect the quality of drinking water and a basic data set for model and projection studies for the protection of drinking water resources will be presented.

Within the scope of this study, the concentrations of heavy metals were determined in the soil samples that were taken seasonally. Soil samples were digested by the BCR sequential extractions methods to examine the chemical forms of heavy metals. The results of this study are summarized as follows.

As total concentrations of heavy metals are examined, the concentrations of Al and Fe are far greater than the other metals, because the soil of Sapanca Lake basin is very rich in terms of these elements that originated from crustal. The mean concentrations of other metals were determined to be Zn>Ba>As>Ni>Cr>Pb>Cu>Co>Cd. Also, heavy metals are mainly found in the residual fraction at all stations. The relationship between the heavy metals in the soil was identified and the significant and positive correlation is observed between Al and Fe ($r^2 = 0.996$), As and Cd ($r^2 = 0.925$) and Ni and Cr ($r^2 = 0.903$). According to RAC, As, Ba and Cd indicate a medium risk in terms of availability of the heavy metals in the environment. Co, Pb and Zn mostly indicate a medium risk and this issue can turn into a medium risk at all stations in the near future. Cd has serious potential ecological risk and As has considerable potential ecological risk at all stations.

Acknowledgements

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