Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 22, Sayı 2, 598-607, 2018

Süleyman Demirel University
Journal of Natural and Applied Sciences
Volume 22, Issue 2, 598-607, 2018

DOI: 10.19113/sdufbed.86744

Applying of Modified Constant Rate of Supply Model to Lake Sediments in ^{210}Pb Dating and Assessment of Some Heavy Metals

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(Alınış / Received: 08.01.2018, Kabul / Accepted: 12.06.2018, Online Yayınlanma / Published Online: 26.06.2018)

Keywords
Sediment accumulation rate,
Modified CRS model,
^{210}Pb,
Pollution load index,
EF values,
Lake Karagöl

Abstract: In present study, Lead-210 (Polonium-210) activity concentrations were indirectly obtained by utilizing alpha spectrometry. Sediment chronology was determined by using modified CRS model. Average sediment accumulation rates are 0.351, 0.324, 0.222 g cm^{-2} y^{-1} in S-1, S-2, S-3 stations respectively. With reference to atmospheric ^{210}Pb flux (29 mBq cm^{-2} y^{-1}) Lake Karagöl has extra outer ^{210}Pb input (soil erosion) from the catchment area. In terms of Enrichment Factor (EF), heavy metal concentrations are lower than the anthropogenic values. So it can be said that the elements except Au originate from the continental supply. Au has unexpectedly too high level EF value (58.22) in northern station (S-1) of the Lake Karagöl. It corresponds to time interval from 2004 to nowadays. However Pollution Load Index (PLI) says different consequences from the EF values. PLI value has only baseline levels of pollutants in northern part of the Lake Karagöl as it shows progressive deterioration of the site for southern part of the Lake Karagöl.

^{210}Pb ile Tarihlemede Modifiye Sabit Akı Modelinin Göl Sedimentlerine Uygulanması ve Bazı Ağır Metallerin Değerlendirilmesi

Anahtar Kelimeler
Sediment birikim hızı,
Modifiye CRS model,
^{210}Pb,
Kirlilik yük indeksi,
EF değerleri,
Karagöl

Özet: Bu çalışmada, Kurşun-210 (Polonyum-210) aktivite konsantrasyonları alfa spektroskopisi kullanılarak dolaylı olarak elde edilmiştir. Sediment kronolojisi modifiye CRS modeli kullanılarak belirlenmiştir. Ortalama sediment birikim hızları S-1, S-2, S-3 istasyonlarında sırasıyla 0.351, 0.324, 0.222 g cm^{-2} y^{-1} dır. Atmosferik ^{210}Pb akısı (29 mBq cm^{-2} y^{-1})'na göre Karagöl, havzasından ekstra dış girdiye (toprak erozyonu) sahiptir. Ağır metal konsantrasyonları Zenginleşme Faktörü (EF) bakımından antropojenik değerlerin altındadır. Dolayısıyla Au hariç elementlerin karasal kaynaklardan meydana geldiği söylenebilir. Beklenmedik biçimde Au, Karagöl'ün kuzey istasyonunda (S-1) çok yüksek EF değerine (58.22) sahiptir. Bu değer, 2004'ten günümüze kadar olan zaman dilimine karşılık gelmektedir. Ancak Kirlilik Yük İndeksi (PLI) durumun EF değerlerinden çıkan sonuçtan farklı olduğunu söylemektedir. PLI değeri, Karagöl'ün kuzey kısmında kirleticilerin sadece baz seviyesine sahipken Karagöl'ün güney kısmı için bölgenin ilerleyici bozunma aşamasında olduğunu göstermektedir.

1. Introduction

The naturally occurring radioactive nuclide Lead-210 (^{210}Pb) has often been used in environmental studies because Polonium (^{210}Po) and ^{210}Pb (half-life is 22.3 y) are well known to be particle reactive in marine environment [1]. ^{210}Po (half-life is 138 d) is an alpha particle emitter in the Uranium-238 (^{238}U) decay chain with high energy and it is a naturally occurring radionuclide formed by the beta decay of its grandparent ^{210}Pb by the agency of Bismuth-210 (^{210}Bi). ^{210}Pb and ^{210}Po have been used extensively as an important tracer for particle transport, studying processes of chemical scavenging, atmospheric analysis, describing the sediment type for pollution point of view (^{210}Po/^{210}Pb ratio), geochronology and dating sediments in marine environment [2]. Especially ^{210}Po is important tool for determining the sediment characteristics and it provides the foresight to radionuclide sorption capability of the sediment. ^{210}Po/^{210}Pb ratio also gives other information on water and sediment columns in lakes, seas and oceans. Determination of this ratio in different type of samples such as in sediment profiles, shallow and

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deep waters, is convenient to obtain the relations between study area and impacts of study area. Investigation of radioactive disequilibria about the pairs ^{210}Po - ^{210}Pb and ^{210}Pb – ^{226}Ra within the oceanic water column determines the rates of scavenging processes [3]. There are two different type of ^{210}Pb supply in coastal (Radon-222) and shelf (Radium-226) waters. Scavenging is important tool to transfer of ^{210}Pb from water column to the sediment layers. ^{210}Pb is also important tool for determining the chronology. Lead dating models [4-9] have entirely applied in lake sediments and they have prosperously improved by new kind of approaches [10-21] to the models for advance correctness of the chronology. Models are commonly derived from the profile distribution of ^{210}Pb activity concentrations. Thus character of the ^{210}Pb distribution is highly descriptive for model choice. Another significand parameter is atmospheric ^{210}Pb flux. Profile distribution of ^{210}Pb is directly affected by the atmospheric ^{210}Pb flux in sediment core [4, 8, 11, 15]. If high supply of ^{210}Pb concentration is existing in any station, it will indicate sediment focusing or significant amount of contribution from the catchment area [22].

Role of the heavy metals which is originating from human activities or from natural contributions is an important impact on environment. Thus pollution investigations are crucial part of geochemical studies [23-25]. According to Nieboer and Richardson [26], some heavy metals are normal constituents of the marine environment. Fe, Cu, Zn, Co, Mn, Cr, Mo, V, Se and Ni are known to be essential to marine organisms, they always function in combination with organic molecules in general proteins. However, Ag, Hg, Cu, Cd and Pb are particularly toxic [27].

The first goal of the present study is to determine the recent chronology in Lake Karagöl by using modified CRS (Constant Rate of Supply) model. Second one is to evaluate the state of lake in term of potential erosion or any other similar effects. Last one is the clarification of metal contamination degree by utilizing the some pollution indexes such as Enrichment Factor (EF), Contamination Factor (CF) and Pollution Load Index (PLI).

There is not any research about sediment dating or sediment accumulation rate especially using modified CRS model, heavy metal pollution degree via Pollution Load Index for Lake Karagöl in literature. To understand the accumulation pattern, the relation between sediment accumulation rates and metal load rates was investigated. ^{210}Pb flux to the lake surface was determined by using core inventories to compare with the global mean ^{210}Pb flux and to detect whether there is erosion. Correlations among metal concentrations were calculated and correlation also was clarified between northern station and southern station in lake.

2. Material and Method

Lake Karagöl is a crater lake and has had the area of 2 km^2. Lake lies between at the 38° 57' 30.8'' N latitude and 26° 50' 55.6'' E longitude. It is about 55 km away from the center of Izmir province. Depth has reached the maximum value at southeastern part with 7.5 meter however it has fallen into 1.8 meter towards north and west part of the lake. Catchment area is closed by native forest which is consists of the pine trees [28]. Sampling stations provide the well representation of the lake in terms of sedimentation pattern, catchment impacts and human activities. These factors were considered in choosing the sampling stations. S-1 is taken place in the northern section of the lake and it is vulnerable to the catchment impacts such as erosion and human activities. S-2 station is taken place in the southeastern part of the lake and it is protected from catchment impacts besides it has maximum water depth. S-3 is taken place in the southwestern section of the lake and it is also protected from catchment impacts and it has minimum water depth.

2.1. Radionuclides

In present work three sediment cores obtained from the Lake Karagöl, one of them is from northern and others are southern part of the Lake in 2015. Figure 1. shows the working area. Depths of the cores vary between 27 and 44 cm. There are two stages in preparation of samples for analysis. First stage is physical preparation. It consists of the following steps. The cores were displaced from the PVC pipes and cut in one cm intervals. Before sediment samples were oven dried, wet weights of the samples noted.

Figure 1. Sampling points and working area [23].

Then they were ground and passed through a 63 µm mesh to reach homogenization. Second stage which is consists of the chemical steps is used for the radiochemical analysis. One gram sediment sample and standardized 0.1 Bq mL^{-1} amount of ^{209}Po (half-life: 103 years) internal tracer (National Institute of Standards and Technology, <500 Bq in 7% hydrochloric acid) were completely dissolved in HF:HNO$_3$ (1:1) and HCl in Teflon beaker. After the ascorbic acid addition, polonium was spontaneously plated onto copper discs in 0.5 M HCl solution. Ascorbic acid was used to reduce ferrum ions [29]. To measure ^{210}Po concentrations 5.30 MeV alpha particle emission which comes from ^{210}Po discs were counted in alpha dedectors (Ortec Octete Plus with 450 mm^2 ULTRA-AS Detectors). After the first deposition of polonium, residual 0.5 M HCl solutions were kept for about sixt months to form of ^{210}Po that was supported ^{210}Pb [30]. Polonium which is formed from ^{210}Pb in the kept 0.5 HCl solution, was plated again onto discs to determine the ^{210}Pb activity. Counting period was adjusted to keep the standard error under the 10% (relative standard error was approximately 5%). The recovery rates of standardized tracer for the sediment samples varied 73% and 86%. Bateman equations and recovery were used to determine ^{210}Po (^{210}Pb) concentrations [31, 32].

In calculation of the sediment accumulation rates, modified CRS (Constant Rate of Supply) model was utilized. Modified CRS model bases on the ratio of the cumulative residual unsupported ^{210}Pb for a given depth to the total unsupported ^{210}Pb activity in the sediment column. The inventory is calculated as below:

$$A(x) = \int_{x}^{\infty} \rho(x) C(x) dx \qquad (1)$$

Where $\rho(x)$ (g cm^{-3}), $C(x)$ (Bq g^{-1}) are the sediment bulk density and excess ^{210}Pb activity at depth x (cm) and $A(x)$ (Bq cm^{-2}) is the cumulative unsupported ^{210}Pb below depth x. For a given depth x the age t (y) of the sediment is calculated like below,

$$t = \frac{1}{\lambda} ln\left(\frac{A_0}{A(x)}\right) \qquad (2)$$

Where A_0 (Bq cm^{-2}) denotes the total inventory of the core. Prevailing sediment accumulation rate (g cm^{-2} y^{-1}) at depth x is calculated as below [33].

$$\omega = \lambda \frac{A(x)}{C(x)} \qquad (3)$$

2.2. Heavy metals

Contamination investigations are of great importance in terms of study area evaluations. To realize the this type of evaluations, normalization is crucial. Thus pollution degrees and enrichment factors (EF) of elements are computed by employing normalization in study area sediments. In general, Al, Sc, Fe, Zr are widely employed in normalization process. Al is commonly utilized choice [31, 34-35] to clarify EFs. It also compensates the fluctuation on both particle size and sediment matrix in coastal sediments [23]. Although Fe is also used in normalization [36-42], Din [43] and Rubio et al. [44] are mentioned that Fe is originated from anthropogenic pollution [45]. Beside of this Sc and Zr are successfully utilized in normalization [46]. EF value is calculated via the formula which is suggested below [47-49]:

$$EF = (C_X/C_{Fe})_S/(C_X/C_{Fe})_C \qquad (4)$$

Where X is any element, C_X/C_{Fe} is the concentration ratio of X to , index (S) is surface layer of sediment column, index (C) is Earth's crust. Beside of this the background values in general could be immediately obtained from the bottom layer [23]. Nolting et al. [50] argues that if EF is higher than 10, it will indicate that sediment is polluted. However some authors [51-53] argue that If EFs varied 0.5 and 2.0 sediments will be independent of human impacts. However they are over 2.0 this implies significant anthropogenic inputs [45]. Anthropogenic factor (AF) values were obtained by using formula [49]. Below;

$$AF = C_s/C_d \qquad (5)$$

Here C_s is the surface layer concentration and C_d is the bottom layer concentration of sediment column [54]. The other name of Anthropogenic factor is Contamination Factor (CF) [40, 55]. In here, C_d value is identified as the 30th layer of sediment column [31]. Contamination factor generally is used in combination with Pollution Load Index (PLI) in evaluation of metal pollution. According to Tomlinson et al.[56];

$$PLI = \sqrt[n]{CF_1 CF_2 \dots CF_n} \qquad (6)$$

For a site where CF contamination factor and n number of metals,

$$PLI = \sqrt[n]{site_1 site_2 \dots site_n} \qquad (7)$$

Where, n is the number of sites for a zone [40]. PLI provides an idea to evaluate a site or zone quality. If PLI is 0.0, it shows perfect quality, 1.0 shows that there is only starting level pollution present and >1 shows acute corruption of the zone. Metal concentrations of the investigated stations were measured via ICP-MS technique in laboratory (Acme) and some standards were (DS9, NIST-981-1Y, NIST-983-1Y) utilized.

In this study, SPSS package program was used to realize the statistical analysis. Variables were the profile distributions of the metals' concentrations. Bivariate correlation analysis was applied to the vertical distributions of metals. Bivariate correlation analysis is a method which points out the magnitude, significance and trend of relation between two variables. In this method, it is unnecessary whether both variables are dependent or independent. Therefore bivariate correlation (two-tailed, pearson correlation) was applied to vertical distributions of metal' concentrations.

3. Results

The total ^{210}Pb activities are ranged from 109.6 ± 8.3 Bq kg^{-1} to 54.2 ± 3.2 Bq kg^{-1} along the core in S-1 station. Similarly, they are ranged from 103.3 ± 4.7 Bq kg^{-1} to 59.7 ± 3.4 Bq kg^{-1}, from 119.5 ± 5.6 Bq kg^{-1} to 59.5 ± 3.6 Bq kg^{-1} in S-2 and S-3 stations respectively.

^{226}Ra activities were designated as 54.2 ± 3.2 Bq kg^{-1}, 59.7 ± 3.4 Bq kg^{-1} and 59.5 ± 3.6 Bq kg^{-1} from the deepest layers of the cores. Unsupported ^{210}Pb activities and their error bars were plotted vs depths and inclination curves were added to the graphs. Fitness between profile distribution of the unsupported ^{210}Pb concentrations and inclination curves was clarified by the regression coefficients in Figure 2. R^2 value is 0.907 in S-1, 0.891 in S-2 and 0.984 in S-3. Therefore in calculation of sediment accumulation rates CRS (Constant Rate of Supply), CIC (Constant Initial Concentration) and CF; CS (Constant Flux; Constant Sedimentation) models are not compatible with each other. Sediment accumulation rates were determined by the modified CRS model. It was preferred rather than the others in all cores due to the R^2 values are lower than the 0.950.

Table 1. Sediment accumulation rates and the chronology by means of the modified CRS model

	S-1 (CRS)				S-2 (CRS)				S-3 (CRS)			
Depth (cm)	SAR ($g\ cm^{-2}\ y^{-1}$)		Year (y)		SAR ($g\ cm^{-2}\ y^{-1}$)		Year (y)		SAR ($g\ cm^{-2}\ y^{-1}$)		Year (y)	
1	0,571	±0,043	2013	±0,1	0,526	±0,024	2013	±0,1	0,297	±0,008	2012	±0,1
2	0,568	±0,024	2011	±0,2	0,558	±0,026	2011	±0,2	0,329	±0,009	2009	±0,2
3	0,592	±0,025	2010	±0,2	0,590	±0,025	2010	±0,2	0,359	±0,010	2006	±0,2
4	0,582	±0,025	2008	±0,3	0,553	±0,022	2008	±0,3	0,357	±0,012	2003	±0,4
5	0,545	±0,023	2006	±0,4	0,501	±0,022	2006	±0,4	0,290	±0,009	2000	±0,5
6	0,544	±0,023	2004	±0,4	0,546	±0,023	2004	±0,4	0,269	±0,009	1997	±0,6
7	0,551	±0,024	2003	±0,5	0,481	±0,020	2002	±0,5	0,290	±0,010	1993	±0,7
8	0,564	±0,025	2001	±0,6	0,465	±0,020	2000	±0,7	0,309	±0,011	1990	±0,9
9	0,536	±0,023	1999	±0,7	0,539	±0,024	1998	±0,7	0,296	±0,011	1987	±1,0
10	0,524	±0,023	1997	±0,8	0,427	±0,018	1996	±0,8	0,243	±0,009	1983	±1,2
11	0,504	±0,022	1995	±0,9	0,403	±0,020	1994	±1,0	0,288	±0,010	1980	±1,3
12	0,482	±0,021	1993	±1,0	0,389	±0,020	1991	±1,2	0,283	±0,010	1977	±1,4
13	0,463	±0,021	1991	±1,1	0,378	±0,018	1989	±1,2	0,221	±0,009	1972	±1,6
14	0,435	±0,020	1989	±1,2	0,337	±0,015	1986	±1,3	0,226	±0,009	1968	±1,9
15	0,410	±0,019	1987	±1,3	0,324	±0,014	1983	±1,4	0,186	±0,008	1963	±2,1
16	0,386	±0,017	1984	±1,4	0,334	±0,016	1980	±1,7	0,164	±0,007	1958	±2,6
17	0,359	±0,016	1982	±1,5	0,300	±0,013	1977	±1,7	0,127	±0,005	1951	±2,7
18	0,334	±0,015	1979	±1,6	0,287	±0,015	1973	±2,2	0,129	±0,005	1944	±2,9
19	0,306	±0,014	1976	±1,8	0,259	±0,013	1970	±2,2	0,104	±0,004	1935	±3,4
20	0,314	±0,015	1972	±2,0	0,239	±0,012	1966	±2,4	0,060	±0,003	1922	±4,3
21	0,297	±0,014	1969	±2,1	0,229	±0,010	1962	±2,4	0,044	±0,002	1905	±4,9
22	0,274	±0,013	1966	±2,3	0,213	±0,010	1957	±2,7	0,021	±0,001	1876	±6,0
23	0,250	±0,012	1962	±2,5	0,166	±0,008	1952	±3,0				
24	0,223	±0,010	1958	±2,6	0,142	±0,007	1946	±3,4				
25	0,207	±0,010	1953	±2,9	0,127	±0,006	1938	±3,8				
26	0,178	±0,008	1948	±3,1	0,127	±0,006	1931	±4,3				
27	0,150	±0,007	1942	±3,4	0,112	±0,005	1924	±4,5				
28	0,121	±0,006	1935	±3,8	0,075	±0,003	1912	±4,7				
29	0,105	±0,005	1926	±4,2	0,050	±0,003	1897	±7,0				
30	0,076	±0,004	1915	±4,7	0,029	±0,001	1874	±6,7				
31	0,062	±0,003	1902	±5,5								
32	0,036	±0,002	1882	±6,6								
33	0,034	±0,002	1861	±8,0								

Element concentrations have measured as Fe > Ca > K > Ti (%), V > B > Tl > Cd (ppm), Au (ppb) in northern part, as Fe > Ca > K > Ti (%), V > B > Tl > Cd (ppm), Au (ppb) in southwestern part of the lake (Table 2.). K, Cd, Tl, and Au are anthropogenically enriched in upper layers of core S-1 but Ca and K are anthropogenically enriched in upper layers of core S-3. Rice of above elements from bottom layer to upper one is not continuous. Table 3. shows correlation coefficients. Figure 3. and Figure 4. display that elevated element values were observed, especially at 1- 7, 14 cm in northern station. It was also observed especially at 5, 16 cm in southwestern station sediment profile.

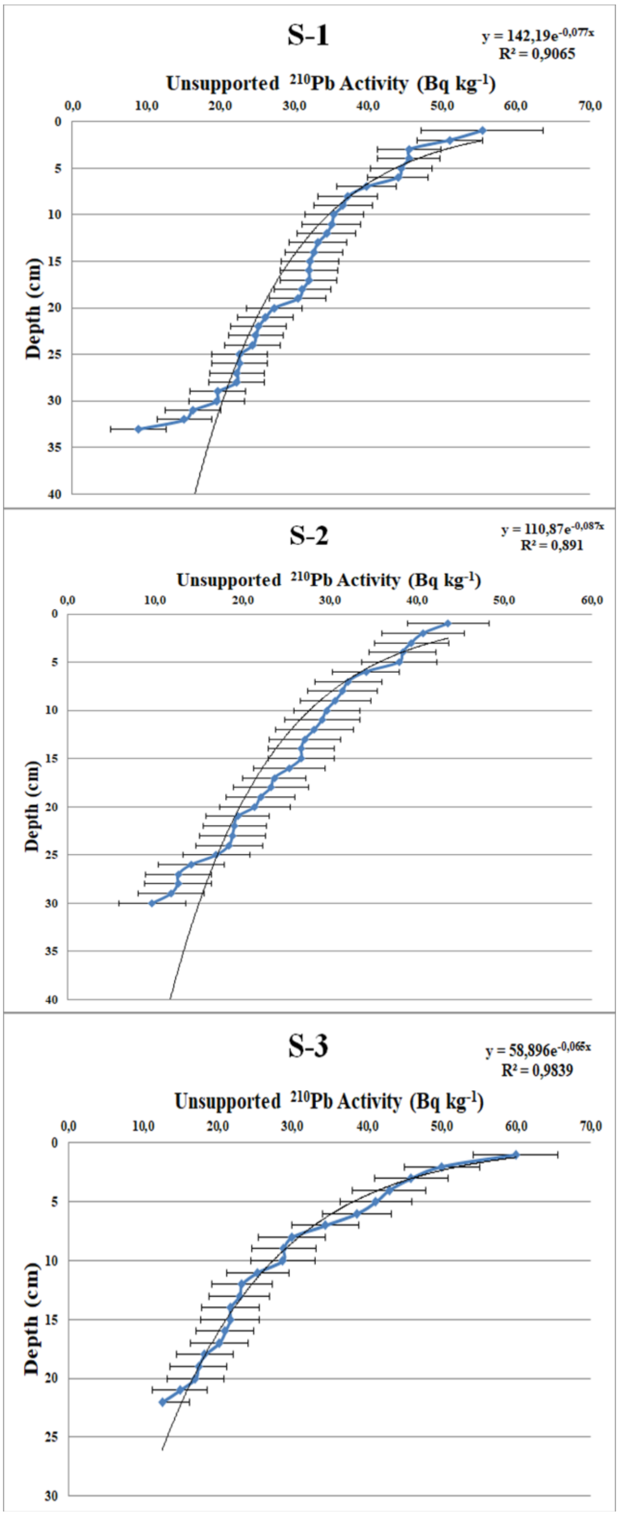

Figure 2. Unsupported ^{210}Pb concentrations

Table 2. Element concentrations in stations

	Fe %	Ca %	K %	Ti %	Cd (ppm)	V (ppm)	B (ppm)	Tl (ppm)	Au (ppb)
S1/0-1	2,79	0,45	0,22	0,13	0,13	91,00	1,00	0,24	11,90
S1/1-2	2,97	0,54	0,25	0,13	0,14	89,00	2,00	0,43	7,90
S1/2-3	2,79	0,44	0,22	0,12	0,07	85,00	2,00	0,26	2,20
S1/3-4	2,70	0,53	0,26	0,12	0,08	83,00	2,00	0,26	2,80
S1/4-5	2,74	0,47	0,21	0,12	0,05	83,00	1,00	0,25	3,40
S1/5-6	2,72	0,49	0,25	0,11	0,05	79,00	2,00	0,31	1,40
S1/6-7	2,69	0,42	0,25	0,12	0,05	77,00	2,00	0,31	2,90
S1/7-8	2,31	0,34	0,18	0,11	0,05	71,00	1,00	0,31	0,50
S1/8-9	2,25	0,35	0,18	0,12	0,07	70,00	2,00	0,28	0,20
S1/9-10	2,51	0,35	0,22	0,13	0,04	80,00	2,00	0,24	0,20
S1/10-11	2,54	0,39	0,23	0,14	0,07	84,00	1,00	0,29	0,30
S1/13-14	2,58	0,38	0,25	0,16	0,07	88,00	3,00	0,31	0,20
S1/15-16	2,65	0,36	0,25	0,16	0,06	91,00	2,00	0,34	0,80
S1/18-19	2,68	0,41	0,21	0,14	0,09	87,00	2,00	0,23	0,60
S1/20-21	2,82	0,40	0,21	0,16	0,03	93,00	2,00	0,22	0,80
S1/24-25	2,63	0,37	0,21	0,14	0,05	88,00	1,00	0,24	0,40
S1/30-31	2,73	0,42	0,19	0,13	0,05	86,00	2,00	0,20	0,20
EF	1	1,05	1,13	0,92	2,54	1,04	0,49	1,17	58,22
AF	1,02	1,07	1,16	0,94	2,60	1,06	0,50	1,20	59,50
PLI	1,70	1,70	1,70	1,70	1,70	1,70	1,70	1,70	1,70
S3/0-1	2,54	0,44	0,23	0,13	0,12	65,00	2,00	0,33	3,20
S3/2-3	2,48	0,45	0,25	0,13	0,13	65,00	2,00	0,36	1,10
S3/4-5	2,53	0,46	0,24	0,14	0,13	66,00	2,00	0,37	1,30
S3/6-7	2,57	0,43	0,22	0,13	0,10	66,00	2,00	0,35	1,80
S3/8-9	2,42	0,44	0,21	0,13	0,10	63,00	1,00	0,35	3,10
S3/10-11	2,59	0,40	0,18	0,13	0,09	69,00	1,00	0,24	0,20
S3/15-16	2,46	0,42	0,19	0,14	0,09	65,00	2,00	0,32	3,50
S3/20-21	2,39	0,35	0,18	0,13	0,13	64,00	3,00	0,31	3,00
EF	1	1,18	1,20	0,93	0,87	0,96	0,63	1,00	1,00
AF	1,06	1,26	1,28	0,98	0,92	1,02	0,67	1,06	1,07
PLI	1,02	1,02	1,02	1,02	1,02	1,02	1,02	1,02	1,02

Table 3. Correlation between elements in stations (P < 0.05*, P < 0.01**)

	Fe	Ca	K	Ti	Cd	V	B	Tl	Au
S-1									
Fe	1								
Ca	0.735**	1							
K	0.493*	0.522*	1						
Ti	0.175	-0.334	0.196	1					
Cd	0.369	0.508*	0.257	-0.043	1				
V	0.737**	0.249	0.351	0.725**	0.288	1			
B	0.113	0.060	0.397	0.321	-0.035	0.105	1		
Tl	0.090	0.253	0.504*	-0.044	0.423	-0.097	0.182	1	
Au	0.540*	0.580*	0.243	-0.182	0.781**	0.311	-0.268	0.241	1
S-3									
Fe	1								
Ca	0.369	1							
K	0.224	0.831*	1						
Ti	-0.022	0.286	0.057	1					
Cd	-0.273	0.059	0.546	-0.043	1				
V	0.832*	-0.026	-0.171	0.044	-0.330	1			
B	-0.381	-0.422	0.021	0.120	0.632	-0.331	1		
Tl	-0.248	0.627	0.783*	0.243	0.501	-0.620	0.264	1	
Au	-0.634	-0.166	-0.191	0.127	-0.029	-0.783*	0.340	0.261	1

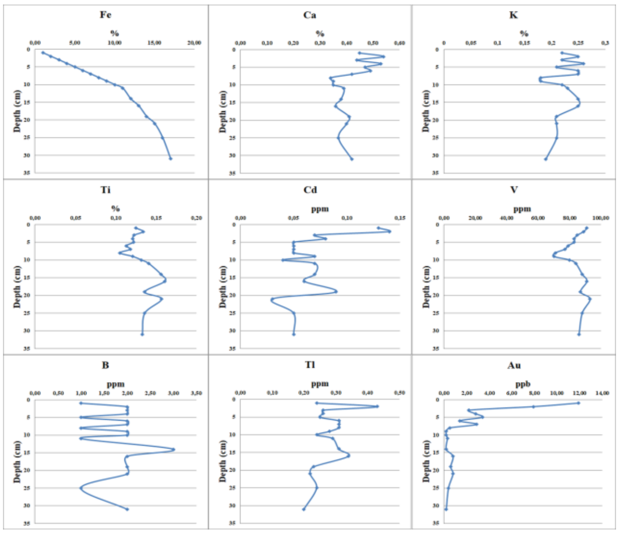

Figure 3. Vertical distribution of metal concentrations in S-1 station

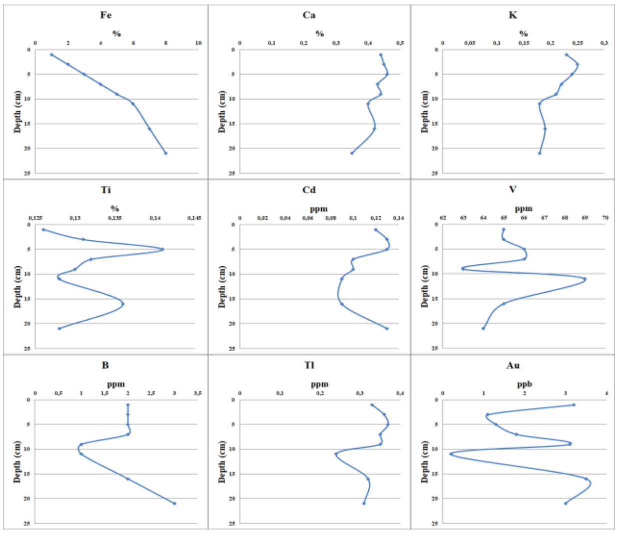

Figure 4. Vertical distribution of metal concentrations in S-3 station

4. Discussion and Conclusion

When supported ^{210}Pb concentration is subtracted from total one concentration for each sediment layer, unsupported ^{210}Pb concentration is obtained. It is utilized in determination of SAR and inventory in cores. By means of the profile distribution of unsupported ^{210}Pb concentrations in Figure 2. R^2 values indicate that ^{210}Pb accumulations to sediment column have shown the nonsystematic pattern in entire working stations.

Sediment accumulation rates ranged from 0.034 ± 0.002 to 0.592 ± 0.025 g cm^{-2} y^{-1} along the core S-1. Sediment accumulation rates (SAR) were given in Table 1. SAR did not reach to hill values. They could be examined in two parts (1, 2). Part 1 has first nine layers of the core. Part 2 has the remaining layers of the core. Lower SARs are seen in Part 2 and range from 1861 to 1991 years but higher SARs are in Part 1 and also range from 2001 to 2013 years. According to the core inventory (941.54 mBq cm^{-2}) ^{210}Pb flux was calculated as 29.28 mBq cm^{-2} y^{-1}. Mean SAR is 0.351 ± 0.016 g cm^{-2} y^{-1}.

S-2 station shows that SAR ranged from 0.029 ± 0.001 to 0.590 ± 0.025 g cm^{-2} y^{-1} in core. SAR displayed noncontinuous decrease from top to bottom levels especially upper eight levels of the core. ^{210}Pb flux and inventory are 21.65 mBq cm^{-2} y^{-1} and 696.13 mBq cm^{-2} in core S-2 respectively. Mean SAR is 0.324 ± 0.015 g cm^{-2} y^{-1} in S-2.

Sediment accumulation rate is lower than the others in S-3 station. It ranged from 0.021 ± 0.001 to 0.359 ± 0.010 g cm^{-2} y^{-1} along the core S-3. SAR also displayed noncontinuous diminish from top to bottom layers especially upper fifteen layers of the core. ^{210}Pb flux and inventory are 19.35 mBq cm^{-2} y^{-1} and 622.20 mBq cm^{-2} in core S-3 respectively. Mean SAR is 0.222 ± 0.008 g cm^{-2} y^{-1}. It is the lowest one in sampling area. SARs have presented in Table 1. for all stations.
Similarly it has differences on ^{210}Pb fluxes which are measured in stations of study area. Krishnaswami and Lal [57], denoted the global mean value of atmospheric ^{210}Pb flux as 165 Bq m^{-2} y^{-1} but Appleby and Oldfield's [58] estimation was 185 Bq m^{-2} y^{-1}. Fluxes which were measured in study area are slightly greater than both the global mean value and Mediterranean field value (75 Bq m^{-2} y^{-1}) [59].

The ^{210}Pb fluxes (296 – 207 Bq m^{-2} y^{-1}) measured from core inventories in Lake Karagöl are higher than Lake Chenghai (average 216 Bq m^{-2} y^{-1}) [60], the average one (43 ± 13 Bq m^{-2} y^{-1}) at Al-Oteibeh Lake [61], Lake Tonček (74 Bq m^{-2} y^{-1}) [62], more or less same with one (1.9 dpm cm^{-2} y^{-1}) at the Sun—Moon Lake in middle Taiwan [63], and lower than Lake Sihailongwan (490 Bq m^{-2} y^{-1}) [64], Red Lake area sediments (309 ± 48 Bq m^{-2} y^{-1}) [65].

Sediment accumulation rates were determined by using Lead-210 model. When glimpsed to the profile distribution of ^{210}Pb concentrations it is seen that R^2 values are lower than the 0.950 for northern and southeastern stations. In addition atmospheric flux is not the dominant factor on controlling the ^{210}Pb supply. Thus in clarifying the sediment chronology modified CRS model was utilized in study area. SAR is generally similar in northern and southeastern stations and higher than it in southwest station. They do not show regular diminish along the cores. By means of Table 3. it is seen that the trend for Fe has a strict correlation with the trend for Ca (0.735**), K (0.493*), V (0.737**), Au (0.540*) in northern station(** $p<0.01$, * $p<0.05$). However the trend for Fe has a strict correlation with the trend for only V (0.832*) in southern station. Similarly Ca has been followed by K (0.522*), Au (0.580*) in S-1 station but it has been followed by only K (0.831*) in S-3 station. Ti has been followed by V (0.725**) in northern station but it has no correlation with other elements in southwestern station. Cd has been followed by Au (0.781**) in S-1 station but it has also no correlation with other elements in S-3 station. V has been negatively followed by Au (-0.873**) in southwestern station. According to above statements it can be said that mentioned elements could be originated from the identical sources in both S-1 and S-3 stations of the lake.

Figure 3. and Figure 4. show that elevated element values in northern and southwestern stations were seen especially at 1-7, 14 cm in S-1 those levels correspond to 2013-2003, 1989 years respectively. Au concentration showed hill values in 1st, 5th, 7th layers of sediment column. They correspond to 2013, 2006, 2003 years with maximum concentrations of 11.90, 3.40, 2.90 ppm respectively. It is not only displays peak values at cited years but also it shows high level concentrations between 2001 and nowadays. The concentration of B reached hill value at 14th cm in the sediment column. It corresponds to 1989 with highest concentration (3.00 ppm). Concentrations of Ca and K displayed high level values between 2004 and nowadays. With respect to Ca concentrations it should be said that biogenic pollution has risen. Thus Ca is mainly derived from biogenic debris. It is known that Ti and V are dominated by terrigenous supply. Their concentrations displayed a decrease between 1984 and 1999, then an increase between 2001 and 2013. There is no relation between sediment accumulation rates and enrichment of metals concentrations inasmuch as metals' concentrations display fluctuation. However sediment accumulation rates do not display similar character with metal concentrations along the core in northern station.

Core S-3 has elevated metal values too. They are especially at 5th, 16th layers of sediment column (Figure 4.) and correspond to 2000, 1956 years respectively. Ti and V show hill values at fifth layer of column. They correspond to 2000 year with concentrations of 0.14 (%) and 66.00 (ppm) respectively. V shows increased value at eleventh layer of column too. It corresponds to 1980 year. Ti also shows increased value at sixteenth layer of column. It corresponds to 1958 year. Neither sediment accumulation rate nor profile distribution of elements is systematic. Therefore it could be said that, the variations of the element concentrations are free from the SARs at southwestern section of the lake too.

Enrichment Factor (EF) is a entirely utilized approach to identify the grade of human impacts on environment [40]. It is a suitable measure to compare pollution with geochemical trends. To fulfil this task there is three reference scale in literature. According to the Nolting et al. [50], an area is polluted by the metals when EFs of the metals are higher than 10. Next, EF values are greater than 5 samples will be considered as polluted [66]. Zhang and Liu [67] argue that, if EF values range from 0.5 to 1.5 metals will originated from Earth's crust. However if EF values are higher than 1.5, metals will probably be related to human activities.

In core S-1, EF values ranged from 1.04 (V) to 58.22 (Au). They are lower than 2 except Au. Like it is mentioned above, there is no input in term of metal pollution except Au. In present work, EF values are evaluated in terms of the successions of Nolting et al. [50]. However PLI value (1.70) indicates progressive deterioration of the site for northern section of the lake.

In core S-3, EF values for Ca (1.18) and K (1.20) indicate that sediments were not contaminated by Ca and K but were rich. PLI value (1.02) also indicates only baseline levels of pollutants present for S-3 station.

In terms of same metal northern station has no statistical correlation with southwestern station in the lake. However, Fe which belongs to S-1 station has a correlation with the B (0.81*) which belongs to S-3. Similarly Ca has a correlation with K (0.71*) and Cd (0.72*), next Ti has a negative correlation with Ca (-0.79*) and K (-0.80*), lastly Tl has a negative correlation with Cd (-0.85**).

Sediment radioisotope dating was realized and element contamination grade of the lake was clarified in present study. To provide the answers for identified tasks, profile distributions of ^{210}Pb activity concentrations and metal concentrations were evaluated. The results show that by means of the profile distribution of unsupported ^{210}Pb, it is seen that ^{210}Pb depositions to the lake is not systematic along the line which lies from northern station to southern station. Similarly ^{210}Pb fluxes calculated from core inventory display the changing character amongst stations and indicate the presence of soil erosion [22]. Because, mean global ^{210}Pb flux is lower than the calculated one. It is known that if measured ^{210}Pb flux is higher than the atmospheric supply rates there will be outer contributions from the catchment area. Apart from this, as to sediment accumulation rates, they are not clearly systematic along the core profiles in all stations (S-1, S-2 and S-3). Mean SAR is 0.299 ± 0.013 g cm^{-2} y^{-1} in study area.

Lake has no relation between SAR and enrichment of elements. Since sediment accumulation rates and metal concentrations along the cores act independent of each other in both northern and southern parts of the lake. According to EF values metals are originated from the crustal (natural) sources in northern and southern sections of the lake. It may be related to the crater lake feature of the Lake Karagöl. Since lake is located the Yamanlar Mountain and Yamanlar volcano has intense internal tectonic deformation [68]. Similarly, AF values indicate that sediments are getting rich on account of some metals but not polluted. Au has interestingly too high level (58.22) EF value in northern station (S-1). It corresponds to time interval from 2004 to nowadays. According to PLI value, northern part of the lake has only baseline levels of pollutants as it indicates progressive deterioration of the site for northern part of the lake. This result is interesting because Lake Karagöl is a natural park and it is protected by natural park rules. The baseline level pollution may be originated from tectonic deformations or human activities because lake catchment has hosted the camping activities. So some more protective precautions should be taken for sustainable environment in Lake Karagöl.

Acknowledgment

Present research study was supported by the Ege University, Science and Technology Centre (EBILTEM). Contract ID: 12NBE007. Author thanks to EBILTEM.

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