

## POLLUTION ASSESSMENT AND STATISTICAL EVALUATION OF RADIONUCLIDES AND METALS IN BOTTOM SEDIMENTS FROM CASPIAN SEA

F.Y. Humbatov<sup>1,2</sup>, S.Sh. Mammadzada<sup>1</sup>

<sup>1</sup>*Institute of Radiation Problems of ANAS*

<sup>2</sup>*University of Architecture and Construction*

[hfamil@mail.ru](mailto:hfamil@mail.ru)

**Abstract:** Metal(loid)s (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Mn, Zn) concentration and activity of radionuclides (Ra-226, K-40, Cs-137) were measured and their correlations in sediment samples collected from 16 sites from Azerbaijani sector of Caspian Sea were investigated to obtain information about pollution and possible sources. To assess pollution in sediments with metals, pollution indices (Geo-accumulation index, Contamination Factor and Enrichment Factor) were calculated. According to calculated values pollution indices, contamination with investigated metals mainly does not pass moderate level pollution. Multivariate statistical analysis methods (Pearson's Correlation Coefficients, Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA)) were used to determine relations between investigated parameters. 4 components were formed as a result of PCA. According to the interpretation of the dendrogram illustrated using HCA method, 4 clusters were formed. Comparison of statistical analysis methods showed that, results are mainly similar. Also, according to the results of correlation analysis, PCA and HCA, Cd has no strong relations with other heavy metals and radionuclides and this could be an indication of a different origin for this element.

**Keywords:** the Caspian Sea, heavy metals, radioactivity, statistical analysis, pollution

### 1. Introduction

The Caspian Sea is a unique natural reservoir on our planet. It is a land locked water body located on the border of two large parts of the continent of Eurasia. The area of the sea is 392,600 km<sup>2</sup> and the sea level lies 27 m below sea level. The Caspian basin hosts a unique ecological system as a result of isolation for over two million years. It is approximately 1200 km long with a maximum breadth of 466 km, contains 79,000 km<sup>3</sup> of water, and has a total coastline of more than 7000 km. The Caspian is fed by five major rivers or river groups: in the north the Volga (80% of total inflow) and the Ural (5%); in the west the Terek, Sulak and Samur (4-5%) and the Kura (7-8%); and, in the south, the short mountain rivers from the Iranian Alborz range (4-5%) [1]. The Caspian sturgeon and the rare fresh water seal are among the most famous of the over 400 species that are endemic to the Caspian Sea. The vast river system and extensive wetlands attract millions of migrating birds and are the habitat of diverse flora and fauna.

Environmental pollution is a major global health threat. Modern technological developments (especially oil and gas production in the Caspian Sea) have brought new challenges concerning environmental safety [2]. In addition to oil production, there are other ways that pollutants enter the waters of the Caspian. The World Bank estimates that one million cubic meters of untreated industrial wastewater are discharged into the Caspian annually.

Numerous contaminants considered as harmful for living organisms such as radionuclides and metals are often analyzed in parts of the ecosystem that tend to accumulate them; namely

soil and sediments [3]. It is well-known that sediments have a great capacity to accumulate and integrate heavy metals and organic pollutants even from low concentrations in the overlying water column [4]. Sediments have been widely used as an environmental indicator and their ability to trace contamination sources and monitor contaminants is widely recognized. Radioactive materials can reach surface waters by various pathways. River water could be contaminated by groundwater or surface runoff of rainwater transporting leached radionuclides from cities, mine waste, deposits, soil weathering, agricultural areas, etc. and could lead to accumulation in sediments [5].

Heavy metal pollutions in the natural environment are a worldwide problem because they are not removed from the water as a result of self-purification and it can accumulate in reservoirs by biological and geochemical mechanisms and enter the biological chain [6]. Heavy metals are poorly soluble in water, so predominantly sorb to suspended particles that then settle as sediment [7]. Heavy metals may accumulate and disturb function in vital organs by binding to cellular components [8].

## 2. Materials and Methods

Sediment samples from the investigated stations were collected by Van Veen grab fitted with stainless-steel jaws. At each station approximately 200 g of sediment sample was taken from the surface oxic layer for metal analysis. Samples were stored in a container that was frozen on returning to the laboratory.

Collected sediment samples were air-dried in the laboratory, disaggregated with a mortar and pestle, and passed through a 2-mm sieve. Particles with a bigger diameter than 2 mm were discarded. Dried, disaggregated, and sieved particles were mixed well and kept in labeled plastic containers for further analysis. Solutions were prepared in deionized water collected from the Milli-Q apparatus (Millipore). Aliquots of approximately 0.25 g of sediment samples were weighed into acid-cleaned TFM vessels and digested with a mixture 6 ml of nitric, 2 ml of hydrochloric and 3 ml of hydrofluoric acid in the microwave oven (Milestone Ethos plus with HPR –1000/10S high pressure rotor). After the dilution process, samples were analyzed using Varian AAS 220 FS+GTA 110+VGA 77 and PerkinElmer AAS AAnalyst 800 with Zeeman corrector to determine heavy metal concentrations.

Sediment samples were analyzed for  $^{226}\text{Ra}$ ,  $^{228}\text{Ra}$ , and other radionuclides ( $\text{K40}$ ,  $\text{Co60}$ ,  $\text{Cs134}$  and  $\text{Cs137}$ ) via gamma-spectrometry using a Canberra intrinsic germanium detector. All gamma spectrometric analyses were performed in silicone sealed 100 ml plastic beakers after aging for one month to allow for ingrowth of  $^{222}\text{Rn}$  and daughters. The photopeaks from the radon daughters  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$  at 295, 352, and 609 keV were used to quantify  $^{226}\text{Ra}$  and the  $^{228}\text{Ac}$  peaks at 338 and 911 keV were used for  $^{228}\text{Ra}$  [9] [10].

## 3. Results and Discussion

Descriptive statistics of the measured parameters for sediment samples including mean, maximum, minimum and also standard deviation all are shown in Table 1. The results showed that the concentrations of these heavy metals and radioactivities of radionuclides in sediments varied in different sampling locations. The average concentrations of investigated heavy metals at the same sampling location followed the order of  $\text{Al}>\text{Fe}>\text{Mn}>\text{Ba}>\text{Cr}>\text{Zn}>\text{Ni}>\text{Cu}>\text{Pb}>\text{Co}>\text{As}>\text{U}>\text{Hg}>\text{Cd}$ .

**Table 1**

## Measured parameters and descriptive statistics of investigated sediment samples

	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Mn	Zn	U	Ra-226,	K-40	Cs-137	Total activity
St.	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	Bq/kg	Bq/kg	Bq/kg	Bq/kg
1	66540	5.26	480	0.131	17.09	111.76	49.03	25106	0.14	54.21	20.24	764	81.62	1.36	16.93	466	8.83	517
2	58180	9.51	511	0.129	16.84	109.36	48.12	23512	0.166	51.43	19.81	755	86.79	1.28	15.90	440	5.81	463
3	64250	7.74	236	0.095	18.37	135.61	55.81	24779	0.064	56.19	15.38	788	79.08	1.5	18.61	463	5.57	511
4	67430	9.19	565	0.142	16.76	92.57	52.59	25678	0.176	52.81	22.52	743	90.41	2.04	25.91	629	23.86	708
5	33804	6.35	277	0.103	19.81	197.44	36.22	22765	0.101	51.19	15.29	814	76.43	1.33	16.56	395	6.23	441
6	67080	7.86	553	0.115	16.91	95.52	52.61	26435	0.198	53.78	22.62	737	93.38	1.97	24.44	598	24.1	681
7	57780	8.49	172	0.097	18.53	108.56	34.03	18538	0.071	51.04	13.23	805	63.44	1.12	13.97	379	2.94	413
8	69870	8.83	498	0.111	15.31	88.96	51.41	26533	0.176	52.37	21.94	654	90.39	1.38	17.10	630	27.12	711
9	63750	9.37	534	0.104	16.53	96.48	52.79	24062	0.156	53.44	18.51	719	83.91	1.72	21.35	508	16.27	574
10	35600	6.04	215	0.082	21.49	294.32	36.04	25327	0.082	52.03	13.87	693	80.74	1.38	17.10	329	3.37	367
11	33820	4.45	61	0.096	7.78	27.68	27.41	7515	0.123	25.18	12.82	372	45.56	0.945	11.74	289	11.69	334
12	64620	8.14	743	0.29	17.76	95.84	62.19	26466	0.148	60.17	19.44	826	89.68	1.77	21.96	611	12.21	680
13	61380	7.21	552	0.109	15.55	83.76	52.63	23101	0.144	52.78	17.52	715	78.73	1.57	19.44	523	10.65	579
14	24690	1.84	158	0.148	7.93	33.44	28.58	8593	0.106	27.18	11.87	392	58.25	0.442	5.49	234	5.42	245
15	61530	8.05	558	0.107	18.13	105.28	54.39	25101	0.09	50.02	16.95	787	80.03	1.76	21.84	540	6.82	595
16	72400	5.32	578	0.122	16.23	103.21	52.41	22654	0.173	53.21	18.43	718	81.35	1.46	18.10	532	11.45	590
min	24690	1.84	61	0.082	7.78	27.68	27.41	7515	0.064	25.18	11.87	372	45.56	0.442	5.49	234	3	245
max	72400	9.51	743	0.29	21.49	294.32	62.19	26533	0.198	60.17	22.62	826	93.38	2.04	25.91	630	27	711
mean	56420	7.10	418	0.12	16.31	111.24	46.64	22260	0.13	49.81	17.53	705	78.74	1.44	17.90	473	11	525
st.dev	15218	2.10	198	0.048	3.65	61.64	10.55	5893	0.042	9.53	3.51	134	12.85	0.395	4.96	122	8	140

**Pollution Indices for Sediments**

To investigate pollution in sediments with heavy metals, Geo-accumulation index (Igeo), Contamination Factor (CF) and Enrichment Factor (EF) were used widely in scientific researches [11] [12]. Pollution indices can be defined as:

$$I_{geo} = \log_2(C_n / (1.5 \times B_n)) \quad (1) [13]$$

$$CF = \frac{C_s}{C_b} \quad (2) [14]$$

$$EF = \frac{(C_s/C_r)}{(C_{sb}/C_{rb})} \quad (3) [15]$$

$C_n$  is the concentration of element "n" and  $B_n$  is the geochemical background value of the element n in the average crust (average upper crustal concentration has been given by Turekian and Wedepohl) [13].  $C_s$  and  $C_b$  are the heavy metal contents in sample and background reference, respectively.  $C_s$  and  $C_r$  are the content of the target element and reference element in the examined sediment respectively and  $C_{sb}$  and  $C_{rb}$  are the content of the target element and reference element in the average shale. Igeo, CF and EF values are calculated with Equation (1), (2) and (3) and results are given in Table 2, Table 3 and Table 4 respectively.

**Table 2**

Geo-accumulation index values of metal(loid)s in investigated sampling points

	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb	As	Cd	Ba	Hg
1	-0.304	-0.606	-1.228	-0.603	-0.379	0.223	-0.300	-0.333	-0.453	-0.043	-0.973	0.900
2	-0.336	-0.623	-1.322	-0.624	-0.455	0.196	-0.212	-0.364	0.401	-0.066	-0.882	1.146
3	-0.025	-0.561	-1.247	-0.498	-0.327	0.410	-0.346	-0.729	0.104	-0.507	-1.997	-0.229
4	-0.576	-0.646	-1.195	-0.631	-0.417	0.324	-0.153	-0.179	0.352	0.073	-0.737	1.231
5	0.517	-0.514	-1.369	-0.390	-0.462	-0.214	-0.395	-0.738	-0.181	-0.390	-1.766	0.429
6	-0.531	-0.657	-1.153	-0.618	-0.391	0.325	-0.106	-0.173	0.127	-0.231	-0.768	1.401
7	-0.346	-0.530	-1.665	-0.486	-0.466	-0.304	-0.664	-0.947	0.238	-0.477	-2.453	-0.079
8	-0.633	-0.830	-1.148	-0.761	-0.429	0.292	-0.153	-0.217	0.294	-0.282	-0.920	1.231
9	-0.516	-0.693	-1.289	-0.651	-0.400	0.330	-0.260	-0.462	0.380	-0.376	-0.819	1.057
10	1.093	-0.746	-1.215	-0.272	-0.438	-0.221	-0.316	-0.879	-0.253	-0.719	-2.131	0.129
11	-2.318	-1.644	-2.968	-1.738	-1.485	-0.616	-1.141	-0.992	-0.694	-0.492	-3.949	0.714
12	-0.526	-0.493	-1.152	-0.547	-0.229	0.566	-0.164	-0.391	0.177	1.103	-0.342	0.981
13	-0.720	-0.701	-1.348	-0.739	-0.418	0.325	-0.352	-0.541	0.002	-0.309	-0.771	0.941
14	-2.045	-1.568	-2.775	-1.710	-1.375	-0.555	-0.787	-1.103	-1.968	0.133	-2.576	0.499
15	-0.390	-0.563	-1.228	-0.517	-0.495	0.373	-0.329	-0.589	0.161	-0.335	-0.755	0.263
16	-0.419	-0.695	-1.376	-0.677	-0.406	0.319	-0.305	-0.468	-0.437	-0.146	-0.705	1.206

**Table 3**

Contamination Factor values of metal(loid)s in investigated sampling points

	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Ba	Pb	Hg
1	1.242	0.899	0.532	0.899	0.797	1.090	0.859	0.405	0.437	0.828	1.012	0.350
2	1.215	0.888	0.498	0.886	0.756	1.069	0.914	0.732	0.430	0.881	0.991	0.415
3	1.507	0.927	0.525	0.967	0.826	1.240	0.832	0.595	0.317	0.407	0.769	0.160
4	1.029	0.874	0.544	0.882	0.777	1.169	0.952	0.707	0.473	0.974	1.126	0.440
5	2.194	0.958	0.482	1.043	0.753	0.805	0.805	0.488	0.343	0.478	0.765	0.253
6	1.061	0.867	0.560	0.890	0.791	1.169	0.983	0.605	0.383	0.953	1.131	0.495
7	1.206	0.947	0.393	0.975	0.751	0.756	0.668	0.653	0.323	0.297	0.662	0.178
8	0.988	0.769	0.562	0.806	0.770	1.142	0.951	0.679	0.370	0.859	1.097	0.440
9	1.072	0.846	0.510	0.870	0.786	1.173	0.883	0.721	0.347	0.921	0.926	0.390
10	3.270	0.815	0.537	1.131	0.765	0.801	0.850	0.465	0.273	0.371	0.694	0.205
11	0.308	0.438	0.159	0.409	0.370	0.609	0.480	0.342	0.320	0.105	0.641	0.308
12	1.065	0.972	0.561	0.935	0.885	1.382	0.944	0.626	0.967	1.281	0.972	0.370
13	0.931	0.841	0.489	0.818	0.776	1.170	0.829	0.555	0.363	0.952	0.876	0.360
14	0.372	0.461	0.182	0.417	0.400	0.635	0.613	0.142	0.493	0.272	0.594	0.265
15	1.170	0.926	0.532	0.954	0.736	1.209	0.842	0.619	0.357	0.962	0.848	0.225
16	1.147	0.845	0.480	0.854	0.783	1.165	0.856	0.409	0.407	0.997	0.922	0.433

**Table 4**

Enrichment Factor values of metal(loid)s in investigated sampling points

	Cr	Mn	Co	Ni	Cu	Zn	Pb	As	Cd	Ba	Hg
1	1.897	1.539	1.535	1.801	2.734	1.902	1.859	1.711	2.273	1.193	4.372
2	1.982	1.624	1.615	1.824	2.865	2.160	1.943	3.303	2.390	1.357	5.535
3	2.332	1.609	1.671	1.891	3.153	1.867	1.431	2.551	1.670	0.595	2.025
4	1.536	1.464	1.471	1.715	2.867	2.060	2.022	2.923	2.409	1.373	5.374
5	3.695	1.809	1.962	1.875	2.227	1.964	1.549	2.278	1.971	0.760	3.478
6	1.540	1.410	1.442	1.697	2.786	2.067	1.973	2.428	1.895	1.306	5.872
7	2.495	2.196	2.253	2.296	2.570	2.002	1.646	3.740	2.279	0.579	3.003
8	1.429	1.247	1.301	1.646	2.713	1.993	1.907	2.718	1.822	1.172	5.200
9	1.708	1.511	1.549	1.852	3.071	2.040	1.774	3.180	1.883	1.385	5.083
10	4.951	1.384	1.913	1.713	1.992	1.865	1.263	1.948	1.410	0.530	2.538
11	1.569	2.504	2.334	2.795	5.106	3.547	3.934	4.836	5.564	0.507	12.832
12	1.543	1.579	1.513	1.896	3.290	1.983	1.694	2.512	4.773	1.752	4.384
13	1.545	1.566	1.517	1.906	3.190	1.994	1.749	2.549	2.055	1.492	4.887
14	1.658	2.307	2.080	2.638	4.656	3.966	3.185	1.749	7.502	1.148	9.671
15	1.787	1.586	1.628	1.662	3.034	1.865	1.557	2.619	1.857	1.388	2.811
16	1.941	1.603	1.615	1.959	3.239	2.101	1.876	1.918	2.346	1.593	5.987

The geo-accumulation index ( $I_{geo}$ ) scale consists of seven grades (0 - 6) ranging from unpolluted to highly pollute. Grade 1 (uncontaminated to moderately contaminated):  $0 < I_{geo} < 1$ ; Grade 2 (moderately contaminated):  $1 < I_{geo} < 2$ ; Grade 3 (moderately to heavily contaminated):  $2 < I_{geo} < 3$ ; Grade 4 (heavily contaminated):  $3 < I_{geo} < 4$ ; Grade 5 (heavily to extremely contaminated):  $4 < I_{geo} < 5$ ; and Grade 6 (extremely contaminated):  $5 > I_{geo}$  [16].

As it can be seen from Table 2,  $I_{geo}$  values of Mn, Fe, Co, Ni, Zn, Pb and Ba in all sampling points; Cr in all points except 5 and 10; Cd in all points except 4, 12 and 14; Cu in points 5, 7, 10, 11 and 14; As in points 1, 5, 10, 11, 14 and 1; Hg in point 3 and 7 are less than 0 meaning mentioned points are unpolluted with these metalloids.  $0 < I_{geo} < 1$  range was observed in point 5 for Cr; for Cu in points 1, 2, 3, 4, 6, 8, 9, 12, 13, 15 and 16; for As in points 2, 3, 4, 6, 7, 8, 9, 12, 13, 15; for Cd in point 4 and 14; for Hg in points 1, 5, 10, 11, 12, 13, 14 and 5. This indicates an unpolluted to a moderately polluted level of contamination.  $I_{geo}$  value of Cr in point 10; Cd in point 12; Hg in point 2, 4, 6, 8, 9 and 16 are in  $2 > I_{geo} > 1$  range indicating moderate pollution.

According to Hakanson [17],  $CF < 1$  indicates low contamination;  $1 < CF < 3$  indicates moderate contamination;  $3 < CF < 6$  indicates a considerable degree of contamination and  $CF > 6$  indicates very high contamination. According to calculated CF values (Table 3), all points are not contaminated with Ni, Mn, Fe, As, Zn, Cd, Hg. Also, CF values of Cr in points 8, 11, 13 and 14; Co in all points except 5 and 10; Cu in points 5, 7, 10, 11 and 14; Ba in all points except 12; Pb in all points except 1, 4, 6 and 8 are under 1 meaning they can be categorized as unpolluted. Mentioned sampling point exceptions with metals above belong to the moderately contaminated class (only Cr in point 16 belongs to a considerable degree of contamination class).

EF<2 indicates that the source of metal is crust materials or natural processes; whereas EF>2 indicates anthropogenic sources [18] [19]. EF<2 indicates minimal enrichment, 2–5 indicates moderate enrichment, 5–20 indicates significant enrichment, 20–40 indicates very high enrichment and EF>40 indicates extremely high enrichment [16]. As it can be seen from Table 4, values of Enrichment Factor range between 5>EF>2 indicating moderate enrichment in the following sampling sites: Cr in points 3, 5, 7 and 10; Mn, Ni and Co in points 7, 11 and 14; Cu in all points except 10, 11 and 14; Zn in points 2, 4, 6, 7, 9, 11, 14 and 16; Pb in points 4, 6, 7, 9, 11, 14 and 16; As in all points except 1, 10, 14 and 16; Cd in points 1, 2, 4, 7, 12, 13 and 16; Hg in 1, 3, 5, 7, 8, 9, 10, 12, 13 and 15. EF values of Cu in sampling points 11; Cd in point 11 and 14; Hg in points 2, 4, 6, 11, 14 and 16 are in the 5>EF>2 range indicating significant enrichment in these points with mentioned metals.

### **Multivariate Statistical Analysis**

Multivariate statistical analyses provide important tools for a better understanding of the complex dynamics of pollutants in the aquatic ecosystems [20]. Pearson's Correlation Coefficients, Principal Component Analysis and Hierarchical Cluster Analysis were applied to determine relations between investigated parameters.

#### **Pearson's Correlation Coefficients**

Correlation analysis provides an effective way to reveal the relationships between multiple variables and thus has been helpful for understanding the influencing factors as well as the sources of chemical components [21] [22]. Pearson's Correlation Coefficients for measured parameters were calculated and results were given in the previous research paper [1].

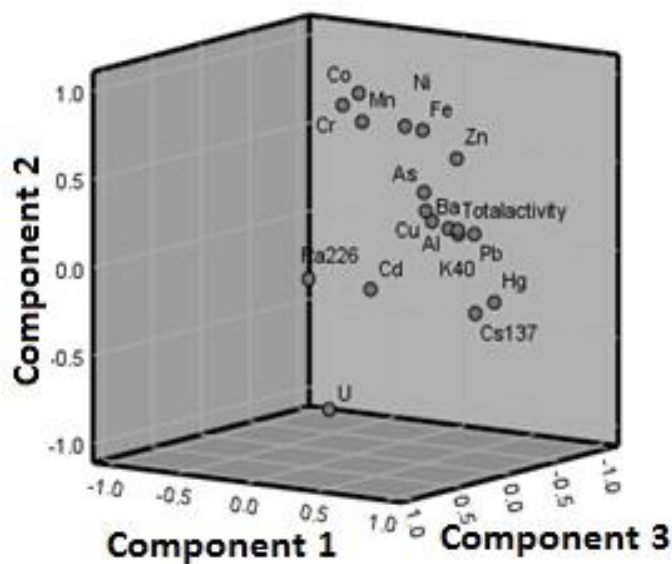
#### **Principal Component Analysis**

Principal Component Analysis (PCA) method have been widely used for the reduction and elaboration of environmental data. To investigate relations between parameters PCA was applied to data. A Varimax rotation (with Kaiser normalization) was applied to the component matrix to clarify the results and to provide a simpler and more meaningful representation of the main factors. Rotation reduces the contribution of variables that have low significance and increases the contribution of the more significant variables. Factor loadings are given in Table 5. 3-dimensional plot of loadings is illustrated in Fig.1. Computations and statistical analysis were carried out using IBM SPSS 25 for Windows. As it can be seen from Table 5, 4 components (with an eigenvalue higher than 1) were formed as a result of the analysis. Factor loading values of Al, As, Ba, Cu, Hg, Pb, Zn, K-40, Cs-137 and total activity is dominant in component 1. Similarly, Co, Cr, Fe, Ni, Mn, U(-) could be categorized in component 2 due to indication values. The highest loading factor value for Ra-226 was observed in component 3. Cd seems to not have a noticeable correlation with other parameters and could be grouped in component 4 for its high negative factor loading.

**Table 5**

Factor loadings for 4 principal components

Parameter	Component			
	1	2	3	4
<b>Al</b>	0.774	0.337	0.321	-0.125
<b>As</b>	0.594	0.458	0.146	0.231
<b>Ba</b>	0.823	0.286	0.221	-0.007
<b>Cd</b>	0.014	-0.192	-0.134	-0.935
<b>Co</b>	0.077	0.960	0.077	0.192
<b>Cr</b>	-0.319	0.794	-0.322	0.231
<b>Cu</b>	0.760	0.401	0.365	0.058
<b>Fe</b>	0.558	0.802	0.109	0.062
<b>Hg</b>	0.674	-0.247	-0.462	0.117
<b>Ni</b>	0.482	0.827	0.182	0.142
<b>Pb</b>	0.897	0.240	0.063	-0.186
<b>Mn</b>	0.279	0.855	0.332	0.117
<b>Zn</b>	0.719	0.640	-0.011	-0.048
<b>U</b>	-0.245	-0.892	-0.075	0.164
<b>Ra-226</b>	0.241	0.030	0.830	0.174
<b>K-40</b>	0.907	0.290	0.245	0.054
<b>Cs-137</b>	0.725	-0.266	-0.194	0.020
<b>Total A.</b>	0.907	0.266	0.242	0.079



*Fig 1. 3-dimensional plot of loadings*

## Hierarchical Cluster Analysis

Cluster analysis can be used to further classify elements from different sources on the basis of similarities in their chemical properties [23]. Hierarchical Cluster Analysis (HCA) was performed to classify elements of different sources on the basis of their similarities and to identify homogeneous variables having similar properties [24] and to evaluate the relation between investigated parameters. HCA analysis was performed via the IBM SPSS software program. A dendrogram was constructed (Fig. 2) to assess the cohesiveness of the determined clusters and to simplify the determination of the correlations between the investigated parameters [23]. It can be seen from Fig. 2, except Cd and U other investigated parameters were grouped in 2 main clusters. K-40, total activity, Pb, Ba, Cu, Al, As, Cs-137 and Hg are forming Cluster 1. Fe, Ni, Mn, Co, Zn, Cr and Ra-226 are in Cluster 2. Cd and U do not have strong relations with other parameters, thus, they form cluster 3 and cluster 4 respectively.

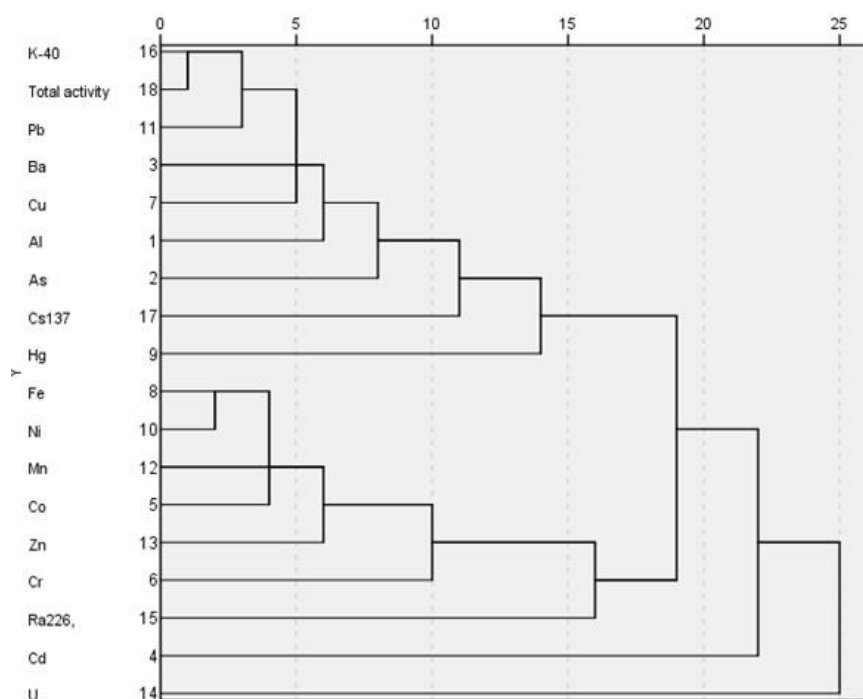


Fig. 2. Dendrogram for hierarchical cluster analysis of investigated parameters in sediments collected from the Caspian Sea.

## 4. Conclusions

Within the present study, heavy metal concentrations and activity of radionuclides were measured for sediment samples collected from the Caspian Sea. The average concentrations of investigated heavy metals at the same sampling location followed the order of Al>Fe>Mn>Ba>Cr>Zn>Ni>Cu>Pb>Co>As>U>Hg>Cd. To assess pollution in sediments with metals, pollution indices (I<sub>geo</sub>, CF and EF) were calculated. According to calculated values of these indices, contamination with investigated metals mainly does not pass moderate level pollution (except Cr in sampling point 16, according to CF value).

Multivariate statistical analysis methods were applied to investigate the correlation between measured parameters. 4 components (with an eigenvalue higher than 1) were formed as a result of Principal Component Analysis. Al, As, Ba, Cu, Hg, Pb, Zn, K-40, Cs-137 and total



activity could be grouped in component 1, Co, Cr, Fe, Ni, Mn, U(-) in component 2, Ra-226 and Cd in component 3 and 4 respectively. Results of HCA showed that, K-40, total activity, Pb, Ba, Cu, Al, As, Cs-137 and Hg are forming Cluster 1; Fe, Ni, Mn, Co, Zn, Cr and Ra-226 are in Cluster 2; Cd and U are forming Cluster 3 and 4 respectively. Results of Pearson's Correlation Coefficients, PCA and HCA were compared to each other. It can be said that the results are mainly similar. Also, according to the results of multivariate statistical analysis methods, Cd has no strong relations with other heavy metals and radionuclides and this could be an indication of a different origin for this element.

## References

1. M. Ahmadov, F. Humbatov. (2018) Determination of radionuclides and metals concentration in Caspian sea sediments. *Journal of Radiation Researches* 5: 442-448.
2. G. Karahan, E. Kapdan, N. Bingoldag, H. Taskin, A. Bassari, A. Atayoglu. (2020) Environmental health risk assessment due to radionuclides and metal(loid)s for Iğdir province in Anatolia, near the Metsamor nuclear power plant. *Int J Radiat Res.* 18 (4) :863-874.
3. Szarłowicz K., Reczyński W., Misiak R., Kubica B. (2013) Radionuclides and heavy metal concentrations as complementary tools for studying the impact of industrialization on the environment. *J Radioanal Nucl Chem.* 298(2):1323-1333.
4. Tam, N. F. Y., & Wong, Y. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. *Environmental Pollution*, 110(2), 195–205.
5. Fetter CW (1993) *Contaminant Hydrogeology*. Macmillan Publishing Company, New York.
6. Loska K and Wiechuła D (2003) Application of principal component analysis for the estimation of source of heavy metal contamination in surface sediments from the Rybnik Reservoir. *Chemosphere* 51: 723–733.
7. Yang J et. al. (2014) Sediment quality assessment for heavy metal contamination in the Dongzhai Harbor (Hainan Island, China) with pollution indice approach. *Open Chem. Eng. J.* 8: 32–37.
8. Landis, D. A., Wratten, S. D. & Gurr, G. M. (2000). Habitat management to conserve natural enemies of arthro-pod pests in agriculture. *Annual Review of Entomology*, 45, 175–20
9. Burnett W et. al. (2002) Assessing Methodologies for Measuring Groundwater Discharge to the Ocean. *EOS* 83: 117-123
10. Landsberger S, Brabeca C, Caniona B, Hashema J, Lua C, Millsapa D and Georgeb G (2013) Determination of <sup>226</sup>Ra, <sup>228</sup>Ra and <sup>210</sup>Pb in NORM Products from Oil and Gas Exploration: Problems in Activity Underestimation Due to the Presence of Metals and Self Absorption of Photons. *Journal of Environmental Radioactivity* 125: 23-26
11. Eneneku A et.al. (2018) Evaluating the potential health risks of heavy metal pollution in sediment and selected benthic fauna of Benin River, Southern. *Appl. Wat. Sci.* 8:224
12. Tytla M and Kosteci M (2019) Ecological risk assessment of metals and metalloid in bottom sediments of water reservoir located in the key anthropogenic “hot spot” area (Poland). *Environ. Earth Sci.* 78: 179
13. Turekian K and Wedepohl K (1961) Distribution of the elements in some major units of the Earth's crust. *Geol. Soc. Am. Bull.* 72: 175-192
14. Tomlinson D, Wilson J, Harris C, Jeffrey D (1980) Problems in the assessment of heavy-metal levels in estuaries and the formation of a pollution index, Helgoland. *Mar. Res.*, 33: 566-575

15. Simex S and Helz G (1981) Regional geochemistry of trace elements in Cheapeake Bay. *Environmental Geology*. 3: 315-323
16. Ho H, Swennen R, Van Damme A (2010) Distribution and contamination status of heavy metals in estuarine sediments near Cau Ong harbor, Ha Long Bay, Vietnam. *Geology Belgica*. 13: 37-47
17. Hakanson L (1980) An ecological risk index for aquatic pollution control, a sedimentological approach. *Water Res.* 14: 975-1001
18. Syrus CP., Michael SA, Lydia LR (2018) Assessing Heavy Metal Contamination in Surface Sediments in an Urban River in the Philippines. *Pol. J. Environ. Stud.* 27(5): 1983-1995
19. Singovszka E and Balintova M (2019) Enrichment Factor and Geo-Accumulation Index of Trace Metals in Sediments in the River Hornad, Slovakia. *IOP Conf. Series: Earth and Environmental Science*, 222.
20. Attia O and Ghrefat H (2013) Assessing heavy metal pollution in the recent bottom sediments of Mabahiss Bay, North Hurghada, Red Sea, Egypt. *Environ. Monit. Assess.* 185: 9925.
21. Evans J (1996) *Straightforward statistics for the behavioral sciences*. Brooks/Cole Publishing, Pacific Grove.
22. Zeng H and Wu J (2013) Heavy metal pollution of lakes along the Mid-Lower Reaches of the Yangtze River in China: Intensity, sources and spatial patterns, *International Journal of Environmental Research and Public Health* 10: 793.
23. Han YM, Du PX, Cao JJ, Posmentier ES (2006) Multivariate analysis of heavy metal contamination in urban dusts of Xi'an, Central China, *Science of Total Environment*, 355: 176-186.
24. Sekabira K, Oryem OH, Basamba T, Mutumba G, Kakudidi E (2010) Assessment of heavy metal pollution in the urban stream sediments and its tributaries. *Int. J. Environ. Sci. Tech.* 7: 435.

## **ОЦЕНКА ЗАГРЯЗНЕНИЯ И СТАТИСТИЧЕСКАЯ ОЦЕНКА РАДИОНУКЛИДОВ И МЕТАЛЛОВ В ДОННЫЕ ОТЛОЖЕНИЯХ КАСПИЙСКОГО МОРЯ**

**Ф.Ю. Гумбатов, С.Ш. Мамедзаде**

**Резюме:** Концентрация металлов (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Mn, Zn) и активность радионуклидов (Ra-226, K-40, Cs-137) и их корреляции в пробах донных отложений, отобранных на 16 участках в Азербайджанском секторе Каспийского моря, были исследованы для получения информации о загрязнении и возможных источниках. Для оценки загрязнения донных отложений металлами рассчитывались индексы загрязнения (Индекс Геонакопления, Коэффициент Загрязнения И Коэффициент Обогащения). Согласно расчетным значениям индексов загрязнения, загрязнение исследуемыми металлами в основном не превышает загрязнение умеренного уровня. Методы многомерного статистического анализа (Коэффициенты Корреляции Пирсона, Анализ Главных Компонентов (АГК) и Иерархический Кластерный Анализ (ИКА)) использовались для определения взаимосвязей между исследуемыми параметрами. В результате АГК образовалось 4 компонента. Согласно интерпретации дендрограммы, проиллюстрированной методом ИКА, было сформировано 4 кластера. Сравнение методов статистического анализа показало, что результаты в основном схожи. Также, согласно результатам корреляционного анализа, АГК и ИКА, Cd не имеет прочных связей с другими тяжелыми металлами и радионуклидами, и это может указывать на различное источника этого элемента.

**Ключевые слова:** Каспийское море, тяжелые металлы, радиоактивность, статистический анализ, загрязнение.

# **XƏZƏR DƏNİZİNİN DİB ÇÖKÜNTÜLƏRİNDƏ METALLARIN VƏ RADİONUKLİDLƏRİN ÇİRLƏNMƏSİNİN QIYMƏTLƏNDİRİLMƏSİ VƏ STATİSTİK TƏDQIQI**

**F.Y. Hübətov, S.Ş. Məmmədzaadə**

**Xülasə:** Xəzə Dənizinin Azərbaycana aid hissəsindən 16 nöqtədən götürülən dib çöküntüsü nümunələrində, mümkün çirklənmə və onun mənbələri haqqında məlumat əldə etmək məqsədilə, metalların (Al, As, Ba, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb, Mn, Zn) konsentrasiyası və radionuklidlərin (Ra-226, K-40, Cs-137) aktivliyi ölçülərək onlar arasındakı əlaqə tədqiq olunmuşdur. Dib çöküntülərində metallarla çirklənmənin qiymətləndirilməsi üçün, çirklənmə indeksləri (Geo-akkumulyasiya indeksi, Çirklənmə Faktoru, Zənginləşmə Faktoru) hesablanmışdır. Hesablanan çirklənmə indekslərinə əsasən, tədqiq olunan metallarla çirklənmənin orta dərəcəni keçmədiyini söyləmək mümkündür. Ölçülən parametrlər arasındakı əlaqəni araşdırmaq məqsədilə, çoxkomponentli statistik analiz metodlarından (Pearson Korrelyasiya Əmsalları, Əsas Komponent Analizi (ƏKA), İyerarxik Çoxluq Analizi (İÇA)) istifadə olunmuşdur. ƏKA nəticəsində 4 komponent formalaşmışdır. İÇA metoduyla əldə olunan dendroqramın təhlilinə əsasən 4 çoxluğun formalaşdığını demək mümkündür. Statistik analiz metodlarının müqayisəsi, nəticələrin əsas etibarilə eyni olduğunu göstərir. Həmçinin, korrelyasiya analizi, ƏKA və İÇA metodlarının nəticələrinə əsasən, Cd-un digər ağır metallarla və radionuklidlərlə güclü korrelyasiyası yoxdur və bu da həmin elementin mənbəyinin fərqli olduğunu indikasiya edə bilər.

**Açar sözlər:** Xəzər dənizi, ağır metallar, radioaktivlik, statistik təhlil, çirklənmə.