Sediment Challenges and Opportunities due to Climate Change and Sustainable Development

Determination of radionuclides and metals consentration in bottom sediment samples taken from the Azerbaijan sector of the Caspian Sea

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Caspian Sea

The Caspian is the largest inland body of water in the world, containing some 44% of the globe's inland waters. The Caspian Sea occupies a deep depression on the boundary between Asia and Europe with a water level at present 27 m below sea level. It is approximately 1200 km long with a maximum breadth of 466 km, contains 79,000 km3 of water, and has a total coastline of more than 7000 km.

Caspian Sea

- 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%).
- Azerbaijan has more than 800 km of coastline along the Caspian Sea and almost the entire country is part of the Sea's catchment area. Environmental problems of the Caspian Sea are multiple and various in their origin. On one hand, they are caused by the commercial use of the sea; on the other hand, human activity impacts coastal areas, including input from rivers in the Caspian.
- As the Caspian is an inland water body, anthropogenic impacts on catchment area (about 3.5 million km2) accumulate here. Anthropogenic impact on the Caspian ecosystem occurs concurrently with various natural endogenous and exogenous processes. It is primarily sea level changes, periodical seismic activity, surges and retreats, mud volcanoes and neo-tectonics.

Sampling and Analysis

- Sediment samples from the stations were collected by Van Veen Grab fitted with stainless-steel jaws. From each station for measurement radionuclides and metals concentration approximately 1000g sample was taken from the surface oxic layer of sediment and stored in a container that was frozen on returning to the laboratory. Sediment samples were analyzed for 226Ra, 228Ra, and other radionuclides (K40, Co60, Cs134 and Cs137) via gamma-spectrometry using a Canberra intrinsic germanium detector. All gamma spectrometric analyses were performed in silicone sealed Marinelli beakers after aging for one month to allow for ingrowth of 222Rn and daughters. The photopeaks from the radon daughters 214Pb and 214Bi at 295, 352, and 609 keV were used to quantify 226Ra and the 228Ac peaks at 338 and 911 keV were used for 228Ra [1].
- Trace metals were determined by AAS 220 FS+GTA 110+VGA 77 firma Varian. All chemicals used were of analytical reagent grade. Deionized water was used throughout the experiment. Stock standard solution (1000 ppm) of heavy metals was purchased from Merck, Germany. The working standard solutions were prepared daily by diluting the stock standard solution of each metal.

Results

Heavy metal concentrations(mg/kg) and radioactivity values(Bq/kg) in sampling points

-	Al	As	Ba	Cd	Co	Cr	Cu	Fe	Hg	Ni	Pb	Mn	Zn	U	Ra^{226},	K-40	Cs137	Total activity
Ст.	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

Results

Comparison of heavy metal concentrations in studied sampling points with EPA standards

Metal (mg/kg)	Not Polluted	Moderately Polluted	Heavily Polluted	Present Study
As	<3	3-8	>8	1.84-9.51
Cd	-	-	>6	0.089-0.29
Co	-	-	-	7.78-21.49
Cr	<25	25-75	>75	27.68-294
Cu	<25	25-50	>50	27.41-62.19
Ni	<20	20-50	>50	25.18-60.17
Pb	<40	40-60	>60	11.87-22.62
Zn	<90	90-200	>200	45.56-93.38
Mn	<300	300-500	>500	372-826
Hg	<1	>-1	>1	0.064-0.198
Ba	<20	20-60	>60	61-743
Fe	<17000	17000-25000	>25000	7515-26533

Results

Pearson Correlation Coefficients

	Al	Fe	As	Ba	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn	U	Tot(A)	Ra	K-40
Al	1.00																
Fe	0.72	1.00															
As	0.66	0.70	1.00														
Ba	0.76	0.70	0.53	1.00													
Cd	0.18	0.13	0.05	0.53	1.00												
Co	0.38	0.83	0.57	0.33	-0.05	1.00											
Cr	-0.17	0.48	0.70	-0.12	-0.26	0.79	1.00										
Cu	**0.86**	0.79	0.62	**0.88**	0.41	0.44	-0.05	1.00									
Hg	0.51	0.29	0.27	0.68	0.23	-0.16	-0.37	0.45	1.00								
Mn	0.61	**0.85**	0.69	0.55	0.15	**0.91**	0.47	0.64	0.00	1.00							
Ni	0.73	**0.95**	0.70	0.67	0.21	**0.87**	0.46	0.78	0.19	**0.93**	1.00						
Pb	0.78	0.71	0.60	**0.83**	0.28	0.28	0.60	0.75	**0.82**	0.45	0.60	1.00					
Zn	0.70	**0.93**	0.65	**0.81**	0.27	0.64	**0.85**	**0.82**	0.54	0.70	**0.85**	**0.87**	1.00				
U	0.71	**0.82**	0.71	0.74	0.17	0.59	0.19	**0.80**	0.43	0.68	0.75	0.73	0.79	1.00			
Tot(A)	**0.86**	0.77	0.67	**0.85**	0.32	0.37	-0.11	**0.87**	0.63	0.56	0.70	**0.88**	**0.81**	**0.86**	1.00		
Ra	0.71	**0.81**	0.71	0.74	0.17	0.59	0.18	0.79	0.43	0.67	0.75	0.74	0.78	1.00	**0.86**	1.00	
K-40	**0.87**	0.78	0.69	**0.87**	0.34	0.39	-0.11	**0.89**	0.62	0.58	0.72	**0.88**	**0.83**	**0.85**	1.00	**0.85**	1.00

Results

- The Pearson correlation coefficients analysis applied to determine heavy metal and radionuclide concentrations of investigated surface sediment samples. Correlation analysis showed strong (R: 0.60-0.79) and very strong correlation (R: 0.8-1) between following group elements: 1) Al-Ba-Cu-As-Ni-Pb-Zn-U-A-Ra-K-40, 2) Fe-Cu-Ni-Zn-U-Ra-226, 3) Co-Fe- Ni-Mn-Zn, 4) Cr-Pb-Zn 5) Hg-Pb-Zn and Ba-Hg ($P < 0.01$ level may be indication of same source)

Results

Principal Component Analysis

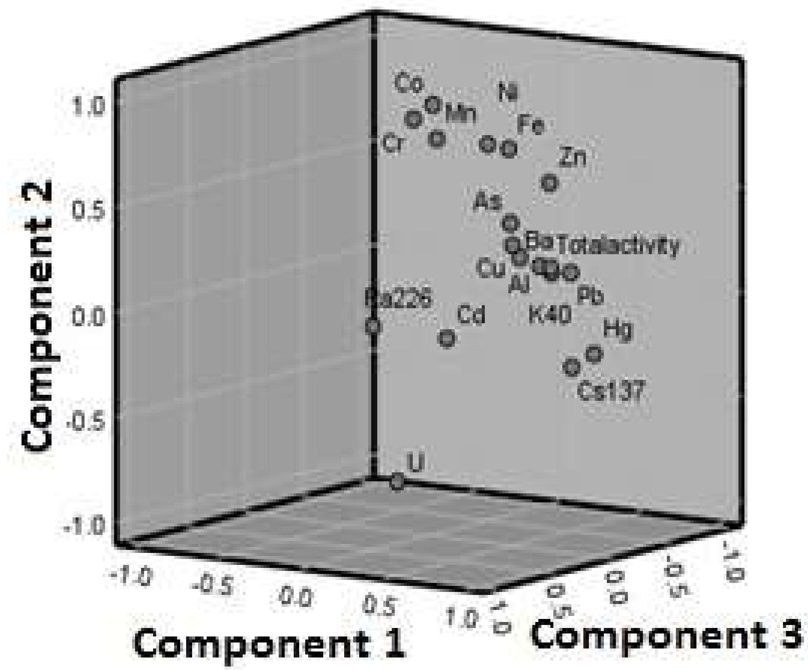
IBM SPSS software was used for application of PCA to data. 4 components (with a eigenvalue higher than 1) were formed as a result of analysis. Indication values of Al, As, Ba, Cu, Hg, Pb, Zn, K-40, Cs-137 and total activity is higher in component 1. Similarly, Co, Cr, Fe, Ni, Mn, U(-) could be categorized in component 2 due to indication values. Highest value for Ra-226 was observed in component 3. Cd seems to not have noticeable correlation with other parameters (according to both Pearson correlation coefficients and result of PCA) and could be grouped in component 4 for its high negative indication value.

Parameter	**Component**			
	1	**2**	**3**	**4**
Al	0.774	0.337	0.321	-0.125
As	0.594	0.458	0.146	0.231
Ba	0.823	0.286	0.221	-0.007
Cd	0.014	-0.192	-0.134	-0.935
Co	0.077	0.960	0.077	0.192
Cr	-0.319	0.794	-0.322	0.231
Cu	0.760	0.401	0.365	0.058
Fe	0.558	0.802	0.109	0.062
Hg	0.674	-0.247	-0.462	0.117
Ni	0.482	0.827	0.182	0.142
Pb	0.897	0.240	0.063	-0.186
Mn	0.279	0.855	0.332	0.117
Zn	0.719	0.640	-0.011	-0.048
U	-0.245	-0.892	-0.075	0.164
Ra226	0.241	0.030	0.830	0.174
K-40	0.907	0.290	0.245	0.054
Cs137	0.725	-0.266	-0.194	0.020
Total activity	0.907	0.266	0.242	0.079

Results

Principal Component Analysis

3 dimensional plot of components

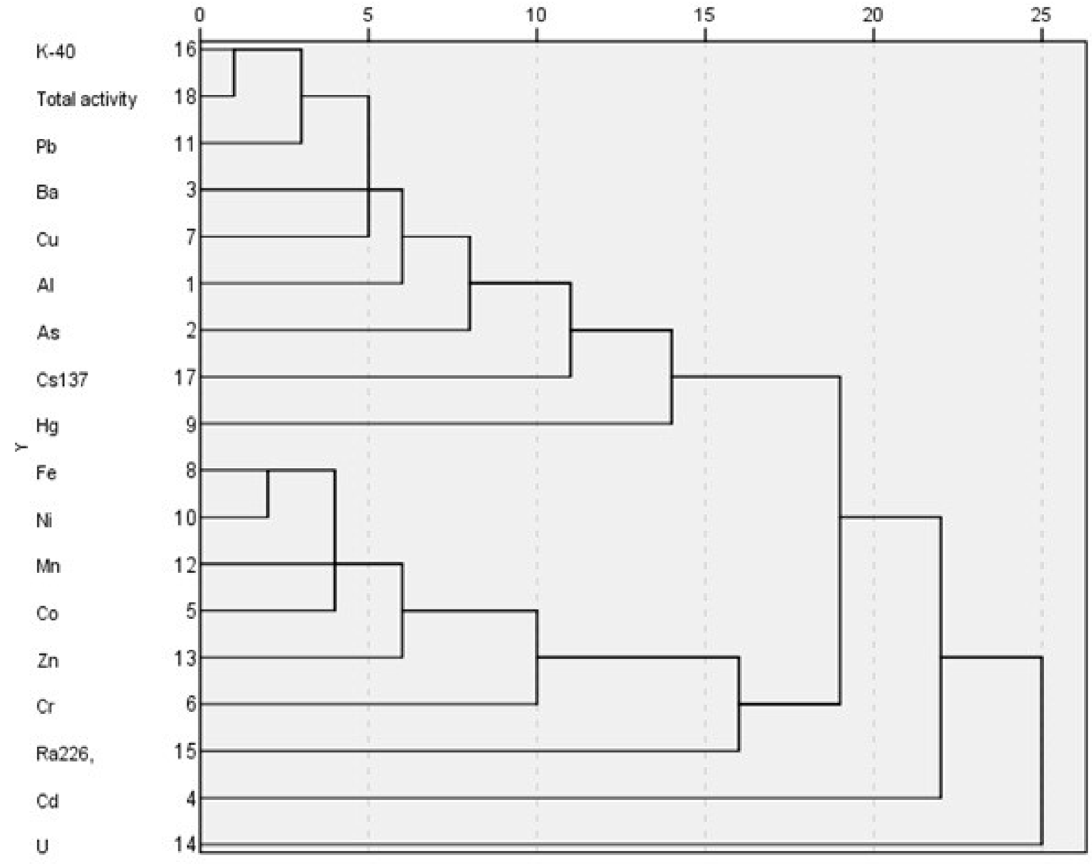


Results

Hierarchical Cluster Analysis

To evaluate relation between investigated parameters Hierarchical Cluster Analysis was used. HCA analysis was performed via IBM SPSS software program. It can be seen from the dendrogram that except Cd and U other investigated parameters were grouped in 2 main cluster. 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.

Dendrogram



Results

- Sediment samples were analyzed for major elements (Al, Fe), heavy metals (As, Ba, Cd, Co, Cr, Cu,Hg, Mn, Ni, Pb, Zn) and radionuclides. The average concentrations of these 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. According to results of analysis, radioactivity levels were in the characteristical level for Sea sediments for naturally occurring radionuclides (Ra226, Th232 and K40). Artificial radionuclides Co-60 and Cs-134 in investigated samples were below MDA but radioactivity of Cs-137 ranges between 0.1-27.1 Bq/kg. It can be explained with quickly dissolving ability of Cs - 137 in water and forming colloids as the ionic form.

Discussion

- The chemical contamination in the sediments was evaluated by comparison with the sediment quality guideline proposed by USEPA. The present study showed that, pollution with As is negligible in one site, moderately pollution was observed in eight site and seven sites were heavily polluted. In all investigated stations pollution with Cd, Pb and Hg belong to unpolluted class. Station 11 and 14 for Cr, stations 1, 2, 5, 10, 11 and 14 for Cu, and station 4 and 14 for Ni can be considered as moderately polluted. All other stations are heavily polluted with noted elements. Concentration of Zn in stations 4, 6 and 8 were greater than 90 mg/kg, sediment samples from all other stations can be considered as not polluted. All stations are heavily polluted with Ba. Possible reason for that could be oil production in Caspian Sea.

Discussion

Similarities among the results of statistical methods (Pearson correlation coefficients, Principal Component Analysis, Hierarchical Cluster Analysis) were observed. According to results of analyzes Al, As, Ba, Cu, Pb, K-40, Tot.act. has strong relations and could have same source and/or transport and accumulation mechanism. Similarly, all statistical method results show that Fe, Ni, Mn, Co, Cr have strong correlation. Cd in the sediments of Caspian Sea do not have strong relation with other investigated parameters. Thus, it can be said that either source of the Cd is completely different from others, or transportation and accumulation in sediments differs. It is known that source of some heavy metals (for example Ba, As) in sea sediments are mainly anthropogenic (oil production). Investigating these heavy metals and their correlations with others could help understand effect of oil production on sea sediments. Considering number of samples in this scientific work, further studies are necessary for such an evaluation.