Determination of radionuclides and elements' concentration in bottom sediment samples taken from the Azerbaijan sector of the Caspian Sea

F.Y. Humbatov[1,2]

[1]Institute of Radiation Problems, ANAS, AZ1143, av.H.Javid 31a,Baku,Azerbaijan Phone: +994-(12)-538-29-57
[2]University of Architecture and Construction, A.Sultanova 11, Baku, Azerbaijan E-mail: hfamil@mail.ru

Introduction:
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 width of 466 km. It contains 79,000 km^3 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%). 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 km^2) 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. Special features of the Caspian include constant alterations of its area, volume, and configuration of the coastline and water column structure. Anthropogenic activity, as well as a natural impact, can have a chronic (long term) or acute (short term) effect. The sources of pollution are industrial, agricultural and accidental discharges and sewage. The main sources of pollution to the Caspian Sea have generally been considered to be offshore oil production and land-based sources, notably the Volga River. In this study concentrations of heavy metals and radionuclides in sediment samples from the Azerbaijan sector of the Caspian Sea were investigated to obtain information about the sources and degree of contaminations.

Methods: Sediment samples from the stations were collected by Van Veen Grab. From each station for measurement radionuclides and metals concentration, approximately 1 kg 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 ^{226}Ra, ^{228}Ra, and other radionuclides (^{40}K, ^{60}Co, ^{134}Cs and ^{137}Cs) 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 ^{222}Rn and daughters. The photopeaks from the radon daughters ^{214}Pb and ^{214}Bi at 295, 352, and 609 keV were used to quantify ^{226}Ra, and the ^{228}Ac peaks at 338 and 911 keV were used for ^{228}Ra [1]. Trace metals were determined by AAS 220 FS+GTA 110+VGA 77, 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: Sediment samples were analyzed for major elements (Al, Fe), minor elements (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn) and radionuclides. The average concentrations of elements 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 the results of the analysis, radioactivity observed for naturally occurring radionuclides (^{226}Ra, ^{232}Th and ^{40}K) is characteristic for sea sediments. Artificial radionuclides Co-60 and Cs-134 in investigated samples were below the minimum detection limit (MDL) but radioactivity of Cs-137 varied in the range of 0.1-27.1 Bq/kg. This can be explained by the quickly dissolving ability of Cs-137 in water and the forming of colloids in its ionic form.

Discussion: The chemical contamination in the sediments was evaluated by comparison with the sediment quality guideline proposed by USEPA. The Pearson correlation coefficients analysis was applied to determine heavy metal and radionuclide concentrations of investigated surface sediment samples. All stations are heavily polluted with Ba and a possible reason for that could be the oil production in the Caspian Sea. Correlation analysis showed strong (R: 0.60-0.79) and very strong correlation (R: 0.8-1) between the following group elements: 1) Al-Ba-Cu-As-Ni-Pb-Zn-U-A-Ra-K, 2) Fe-Cu-Ni-Zn-U-Ra, 3) Co-Fe- Ni-Mn-Zn, 4) Cr-Pb-Zn 5) Hg-Pb-Zn and Ba-Hg (correlation at the $p < 0.01$ level may be an indication of the same source).

References:
[1] F. Y. Humbatov et al.(2016) J Environmental Protection 7:1149-1156