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CHEMICAL COMPOSITION AND NATURAL RADIOACTIVITY OF BEACH SANDS FROM THE ADRIATIC SEA COASTLINE, ALBANIA

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Abstract. *The Adriatic coastline (Shëngjini bay, Lalzi bay, Durrës bay and Spille bay) is previously investigated for the activity concentration of natural radionuclides in sand samples by means of high-resolution gamma ray spectrometry technique. The highest activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th are found to be 458 Bq/kg, 67 Bq/kg and 91 Bq/kg, respectively. This study aims to investigate the dose rate and elemental composition of beach sands in order to better understanding of the behaviour of radionuclides in the coastline of the Adriatic Sea in Albania. The same sand samples are characterized for the chemical composition by means of X-ray fluorescence spectrometry (XRF) together with some REEs (rare earth elements). A good correlation is found between natural radionuclide concentration and REEs in general giving a good indication on weathering conditions in the region. In particular, the highest concentration of REEs is measured for the same sample showing the highest concentration of natural radionuclides. Therefore, this area is investigated for the gamma dose rates by direct measurements using identiFINDER® 2, a handheld instrument. Results indicate layered deposits of showing relatively higher dose rates and confirming the presence of heavy minerals. However, it is required to obtain further information about geology and geochemistry of this area for investigating the mineralogy and origin of these deposits.*

Keywords: *natural radioactivity, chemical composition, XRF, REEs, gamma dose rate*

1. Introduction

Beach sands are formed from the erosion and weathering of rocks, which may have different concentrations of natural radionuclides. The coastline of the Albanian Adriatic Sea has been previously studied to assess the concentrations of natural radionuclides and evaluate their radiological health risk, indicating its significant radiological health risk to the population and tourists [1]. The average activity concentrations of ^{40}K, ^{226}Ra and ^{232}Th are found to be 238 ± 89 Bq/kg, 14 ± 5 Bq/kg and 11 ± 5 Bq/kg, respectively. However, higher concentrations are found to be up to 458 Bq/kg, 67 Bq/kg and 91 Bq/kg, respectively for ^{40}K, ^{226}Ra and ^{232}Th. Several studies in other countries in Adriatic Sea region have investigated the concentrations of natural radionuclides in beach sands [2, 3, 4].

Very few studies relate some of these areas in the Albanian Adriatic Sea coastline to heavy mineral placers such as zircon, rutile, ilmenite, garnet, magnetite, titan-magnetite and chromite [5]. These minerals typically have significant levels of Rare Earth Elements (REE) together with uranium and in particular thorium. Several studies indicate a significant relationship between placer deposits and natural radionuclides [6, 7]. Therefore, the same sand samples from the Adriatic Sea coastline characterized earlier for the radionuclide concentration are additionally characterized for their chemical composition by means of X-ray fluorescence spectrometry (XRF), together with some REEs (rare earth elements).

2. Materials and Methods

Sand samples were collected along the Adriatic Sea Coastline (beach of Shëngjini bay, Lalzi bay, Durrës bay and Spille bay). Twenty samples were collected from a depth of 5-20 cm, and each sample weighting around 1 kg. Previously collected and prepared samples are further processed and transformed into thick pressed pellets after being re-dried overnight at 105°C and ground into fine powder (<200 mesh).

Measurements were performed using two experimental EDXRF systems. The first, which uses secondary target excitation mode, consists of a Philips 1729 X-ray generator equipped with a Mo-anode X-ray tube and a 30 mm² PGT Si(Li) detector used to measure elements between K and Zr. The second system consists of an Am-241 excitation source and an 80 mm² PGT planar HpGe detector used to measure elements between Sn and Nd. Both systems use a compact, 90° source-sample-detector geometrical setup designed and prepared in the laboratory. A thin filter of Mo and Pb respectively was placed between the target/source and the sample to filter the primary radiation. The program AXIL [8] calculated the intensities of the characteristic X-ray lines of the elements. The program COREX [9], which uses backscattered peaks and

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fundamental parameters, was used for calculating the concentrations of the elements excited by the Mo secondary target. The concentrations of Ba, La, Ce and Nd excited by the Am-241 source, were calculated using the Compton scattered peak as an internal standard [10]. In both cases the necessary initial calibrations were obtained through direct measurement of a set of standards prepared from pure elements or compounds. A set of internationally recognized standard reference materials, mainly of soil or sediment origin, was used as primary standards for monitoring the precision and analytical accuracy [11].

3. Results and Discussion

The chemical concentrations in beach sand samples measured using EDXRF technique are reported in Table 1. Figure 1 shows the correlation of potassium concentrations measured in beach sand samples by using gamma-ray spectrometry and EDXRF methods. The Pearson correlation coefficient 0.925 shows a very good agreement between the two methods.

Table 1. Chemical content in beach sands, as obtained through EDXRF analysis.

Sample ID	K (%)	Ca (%)	Ti (%)	Fe (%)	Cr (ppm)	Mn (ppm)	Ni (ppm)	Zn (ppm)	Br (ppm)	Rb (ppm)	Sr (ppm)	Y (ppm)	Zr (ppm)	Pb (ppm)	Th (pmm)	Ba (ppm)	La (ppm)	Ce (ppm)	Nd (ppm)
GJS-1	**0.17**	9.87	1.72*	**9.39***	**27679***	**2679***	**837***	**160***	15	**6**	177	45*	80	< 20	20	**33**	32*	70*	34*
GJS-2	0.73	9.80	0.64	4.75	12965*	1204	466	75	12	17	158	22*	274	< 20	18	222	19	39	23
GJS-3	0.53	13.08	0.30	3.29	4652*	1053	410	35	12	14	164	12	89	< 20	< 15	120	16	28	14
GJS-4	0.92	10.78	0.23	2.79	2227	965	421	26	7	18	147	11	96	< 20	< 15	159	13	25	**11**
GJS-5	0.67	11.78	0.19	2.51	1432	901	348	15	13	13	143	11	65	< 20	< 15	138	13	21	12
GJS-6	0.94	9.04	0.20	2.50	779	802	387	20	13	22	148	13	91	< 20	< 15	170	13	21	12
GJSH-1	1.23	**6.33**	0.37	4.31	789	1098	265	60	7	**47**	137	15	90	27	20	181	20	37	19
GJSH-2	1.19	7.17	0.40	4.74	2036	1146	266	64	11	37	142	18	107	< 20	< 15	158	18	39	21
GJSH-3	0.96	8.33	0.27	3.43	474	919	232	49	11	33	167	14	107	28	< 15	142	14	28	15
GJV-1	0.76	9.96	0.27	3.55	445	1001	229	42	11	20	179	16	117	< 20	< 15	95	13	24	13
GJV-2	0.75	7.43	0.23	2.88	345	832	252	28	7	15	**134**	13	86	< 20	< 15	103	13	24	12
GJV-3	1.02	8.18	0.35	3.91	1224	964	234	51	12	40	155	13	**25**	< 20	16	136	15	30	17
GJD-1	1.62	6.86	0.25	1.26	795	539	66	17	13	40	162	11	129	< 20	21	**417**	19	32	16
GJL-1	**1.65**	8.95	**0.08**	**0.35**	**60**	**258**	**25**	**10**	8	42	258	10	25	< 20	< 15	360	**11**	**16**	12
GJL-2	0.97	16.18	0.21	1.23	1641	736	81	14	9	28	278	10	74	< 20	< 15	265	14	24	13
GJL-3	0.89	7.30	**1.89***	3.53	15313*	2271*	25	56	12	32	240	**58***	**639***	24	23	191	**107***	**204***	**80***
GJL-4	1.02	**20.05**	0.54	2.02	6766*	1184	70	39	**5**	20	**322**	**10**	253	< 20	< 15	403	24	46	24
GJL-5	0.87	15.10	0.28	1.40	1889	776	83	21	11	24	287	10	123	< 20	< 15	263	15	30	16
GJL-6	0.91	14.02	0.12	0.96	117	685	70	10	6	25	271	10	25	< 20	< 15	203	12	20	12
GJL-7	1.03	13.26	0.17	1.37	291	711	84	15	**18**	29	266	10	91	29	< 15	243	13	24	13
Range	**0.17 – 1.65**	**6.33 – 20.05**	**0.08 – 1.89**	**0.35 – 9.39**	**60 – 27679**	**258 – 2679**	**25 – 837**	**10 – 160**	**5 – 18**	**6 – 47**	**134 – 322**	**10 – 58**	**25 – 639**	/	/	**33 – 417**	**11 – 107**	**16 – 204**	**11 – 80**

* identify the outliers.

Table 2. Pearson correlation coefficients between HPGe and EDXFR data calculated after rejecting the outliers.

EDXRF	K HPGe (%)	U HPGe (ppm)	Th HPGe (ppm)
K (%)	0.925	-0.129	0.124
Ca (%)	-0.228	0.242	-0.105
Ti (%)	-0.368	0.848	0.933
Fe (%)	-0.504	0.224	0.593
Cr (ppm)	-0.321	0.340	0.322
Mn (ppm)	-0.757	0.472	0.654
Ni (ppm)	-0.593	-0.019	0.135
Zn (ppm)	-0.338	0.544	0.811
Br (ppm)	-0.129	-0.011	-0.119
Rb (ppm)	0.800	-0.116	0.251
Sr (ppm)	0.225	0.220	-0.130
Y (ppm)	-0.253	-0.062	0.429
Zr (ppm)	-0.264	0.814	0.724
Pb (ppm)	/	/	/
Th (ppm)	/	/	/
Ba (ppm)	0.683	0.300	0.208
La (ppm)	-0.090	0.836	0.906
Ce (ppm)	-0.230	0.861	0.968
Nd (ppm)	-0.154	0.888	0.948

Note: red – non significant very small to small relationship, yellow - non significant to significant medium relationship, and green - significant large relationship.

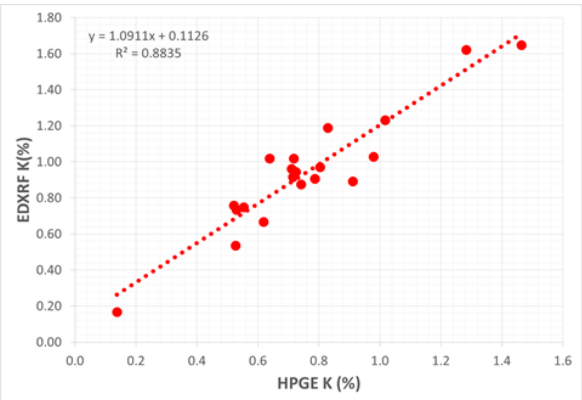

Figure 1. The correlation of the potassium concentrations measured using HPGe and EDXRF methods.

The samples GJS-1 and GJL-3 show the most frequent outliers (i.e. exceeding the median of ±1.5 Interquartile Range) in the respective distribution of chemical content. In Figure 2, the normalized chemical composition is reported as indicated for the upper continental crust [12], which emphasizes the enrichment of chemical elements in these samples. GJL-3 samples correspond to the highest activity concentrations of 226Ra and 232Th measured, at 67 Bq/kg and 91 Bq/kg, respectively. It seems that the main contributors to radionuclide enrichment in beach sands are due to the presence of heavy minerals. The presence of the heavy minerals along the shore in the Adriatic Sea and especially in this area (GJL-3), has been previously been reported by Ostrosi et al. [5].

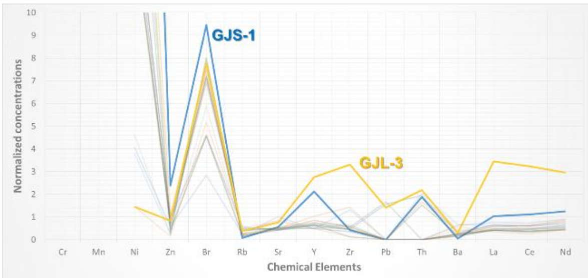

Figure 2. The normalized chemical composition referring to the upper continental crust.

In Figure 3, the correlation between uranium and thorium measured by gamma-ray spectrometry and some of the most representative chemical elements measured by EDXRF is shown. The Pearson correlation coefficients were calculated after rejecting the outliers from the statistical analysis and found to be 0.800 (K vs. Rb), 0.814 (U vs. Zr) and 0.968 (Th vs. Ce) showing a significant correlation between these elements. The Pearson correlation coefficients are summarized in

Table 2, demonstrating a significant large relationship between heavy metals and radionuclide concentrations.

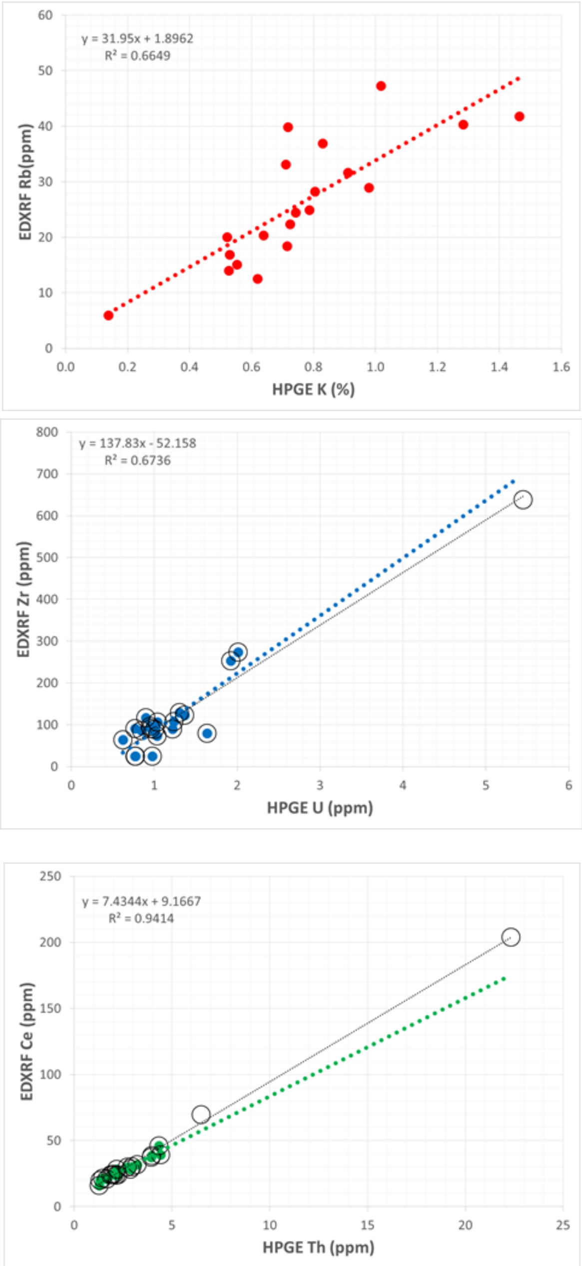

Figure 3. The correlation between K and Rb (top figure), the correlation between U and Zr (middle figure), and the correlation between Th and Ce (bottom figure). The hollow circles indicate the data including the outliers.

Field investigation of the gamma dose rates by direct measurements using identiFINDER® 2, indicates layered deposits showing relatively higher dose rates (increasing from 54 nGy/h to 82 nGy/h) which suggest the presence of heavy minerals.

5. Conclusion

This study presents the results of the survey of chemical composition and discusses them in correlation with natural radioactivity in the sands of touristic beaches along the Adriatic Sea, Albania. Results show increase in chemical elements in few samples, corresponding to the highest values reported for ^{226}Ra and ^{232}Th concentrations. The Pearson correlation coefficients show a significant large relationship (higher than 0.8) between heavy minerals (e.g. Zr) and REE (e.g. La, Ce, Nd) and natural radioactivity. These results confirm the presence of heavy minerals and REE previously reported in the literature. Indeed, layered deposits are confirmed by field measurements of the gamma dose rates. Further information is needed about the geology and the geochemistry of this area to investigate the mineralogy and origin of these deposits.

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