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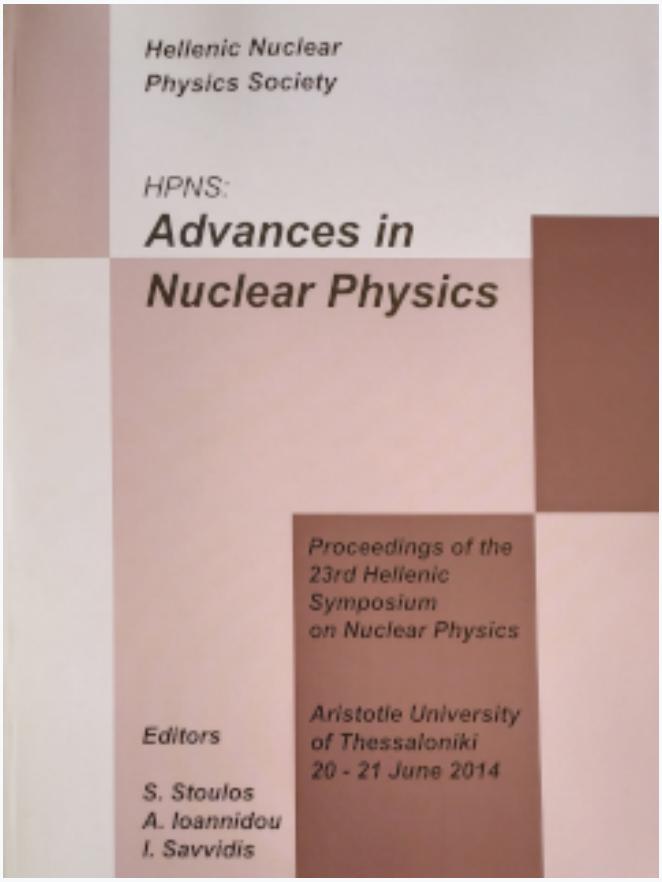

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Radiotoxic metals concentration measurement in sediments due to gold mining activities, Chalkidiki.

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Abstract
The mining operation and tailing deposits in Stratoni region, Northern part of Greece, make monitoring activities necessary both in the terrestrial and coastal areas. As a part of a preliminary monitoring action, in summer of 2012, surface sediment samples in the coastal area of Stratoni (in Ierissos Gulf) were collected and measured aiming a) to obtain concentration levels of (Natural Occurring Radioactive Materials) NORM and heavy metals (e.g. As, Zn, Cu, Pb and Mn,), b) to identify minerals composition and c) to determine the distribution of the grain size. The activity concentrations of ^{238}U, ^{232}Th daughters and ^{40}K were found between (20-100) Bq/kg, (20-35) Bq/kg and (420-700) Bq/kg, respectively. The concentrations of the most toxic heavy metals were found, (8-4100) ppm for As, (30-4000) ppm for Zn, (7-200) ppm for Cu, (40-1700) ppm for Pb and (400-26000) ppm for Mn. In addition, granulometric analysis reveals mostly sandy and sandy-mud sediments (97 – 53% content of sand). In general, enhanced levels of heavy metals and radionuclides were located near the load-out pier area of the coastal region. So, the input mechanisms of them (via local streams, rainfall, floods or others) into the sea and their levels has to be periodically investigated through more concerted monitoring actions.

1. Introduction

From the anthropogenic activities, special attention must be paid to mining, as it may not only affect the soil locally but can also have a wider impact to the aquatic ecosystems due to mining-milling operations, acid mine drainage, erosion of waste dumps and disposal of tailings. (Salomons, 1995; Allan, 1997; Razo *et al.*, 2004).

The mining activity in Stratoni has a long history, dating back to 600 BC, with a mining and metallurgical peak in the 70's. The monitoring of the region was held primarily by the exploration company (Kelepertzis *et al.*, 2006; Kelepertzis *et al.,* 2012; Lazaridou *et al.*, 2004) and to a lesser extent by personal initiative (Stamatis *et al.*, 2002; Sakellariadou, 1987), emphasizing on heavy metal concentrations. The solid wastes of the exploration and the metallurgical processes are deposited at various locations between Stratoni and Stratoniki, along the streams of Stratoni area (Kelepertzis *et al.*, 2006; Charalampides *et al.*, 2013).

The main objective of this work is to provide a baseline information on radioactivity levels (NORM) and heavy metal concentrations in the coastal sediments of Ierissos Gulf. Special interest was paid to sediments due to their ability to accumulate metals and remove them from the water column.

2. Materials and methods

2.1 Study area

The Stratoni area is situated in the Chalkidiki Peninsula, northern Greece (Fig. 1). The study area lies between latitudes 40^{o} 30' and 40^{o} 32.5' and longitudes 23^{o} 45' and 23^{o} 32.5'

Fig. 1 Map of the study area and the sampling locations

Nine surficial marine sediments were collected from Ierissos Gulf (S 1-9). The study area was divided into the following regions: a) region I in Stratoni port near the load out pier area (S4), b) region II in Stratoni port close to the load out pier area (S 1, 2, 3, 5, 6), c) region III close to Kokkinolakkas River estuary (S7, S8) and d) region IV in Ierissos port (S9). Site S9 was chosen as reference location for the study of the potential influence of the industrial activities (Stratoni port) and the estuary on the near-shore sediments of the gulf. The sampling locations coordinates are presented in Table 1. Additionally, measurements of oceanographic parameters (e.g. salinity, temperature), were obtained at the sampling locations by means of a portable CTD (Conductivity-Temperature-Depth) instrument (Table 1).

Table 1. In situ measurements using a CTD instrument (Conductivity-Temperature-Depth)

Region	Sample	Latitude	Longitude	Depth (m)	Temperature (^{o}C)	Salinity (‰)	Density (kg/m^3)	Conductivity (S/m)
I-Load	**S4**	40°30.930' N	023°49.870' E	-	-	-	-	-
II-Stratoni port	**S1**	40°30.390' N	023°49.840' E	0	26.9	34.2	22.1	5.39
				20	21.4	35.9	25.1	5.05
	S2	40°30.640' N	023°49.940' E	0	26.7	34.4	22.4	5.40
				20	19.6	26.4	18.3	3.69
	S3	40°30.850' N	023°50.050' E	8	26.5	28.8	18.2	4.60
				22	20.5	29.6	20.6	4.17
	S5	40°30.690' N	023°49.780' E	6	-	-	-	-
	S6	40°30.410' N	023°49.560' E	4.8	27.2	22.7	13.4	3.76
III-Estuary	**S7**	40°28.070' N	023°49.590' E	2.4	27.2	34.5	22.2	5.46
	S8	40°26.990' N	023°50.110' E	2.3	26.9	34.0	22.0	5.38
IV-	**S9**	40°23.900' N	023°53.102' E	3.4	26.8	34.6	22.4	5.43

2.2 Methodology

The samples were drained, sieved and pulverized in order to achieve an homogeneous powder with maximum grain size 63μm. Then they were placed and closed in specific airtight boxes. The measurements were carried out by means of an ORTEC co-axial 50% HPGe detector. The activity concentration of the samples was derived in Bq/kg from the gamma ray spectra using the SPECTRW spectrometry software package (Kalfas, 2011) and the (2.1) formula.

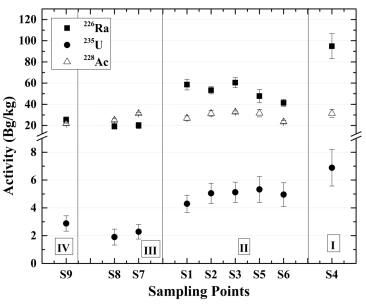
$$Activity = \frac{counts}{eff \cdot \tau \cdot m \cdot I_\gamma} \qquad (2.1)$$

Where t, is the time measurement of each sample (24 h), $e_{ff,}$ the absolute efficiency of the detector, m, the mass of each sample and I_γ, the gamma ray intensity for the energies of interest.

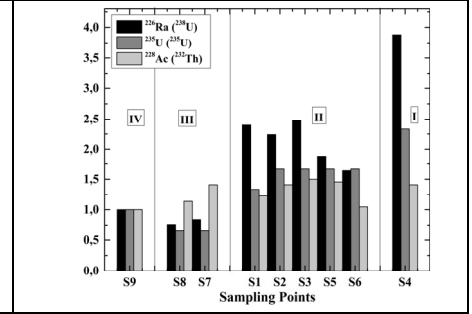
The heavy metals concentration measurements were analysed by XRF (X-Ray Fluorescence) method. For this method, a 5gr mass of well pulverized sample is needed is measured using a Wavelength Dispersive X-Ray Fluorescence system (WDXRF) (Karageorgis *et al.*, 2005). The heavy metal concentration is given in ppm.

3. Results

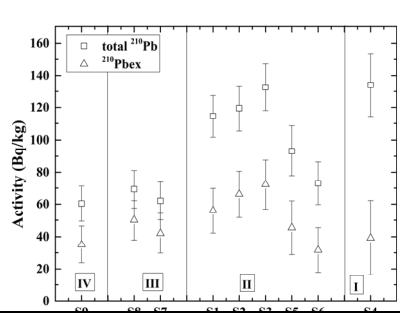
The results of activity (^{210}Pb, ^{210}Pb$_{ex}$, ^{226}Ra, ^{235}U, ^{228}Ac and ^{40}K) and metal (As, Zn, Pb, Cu and Mn) concentrations are depicted to the diagrams (Fig. 2, 3).



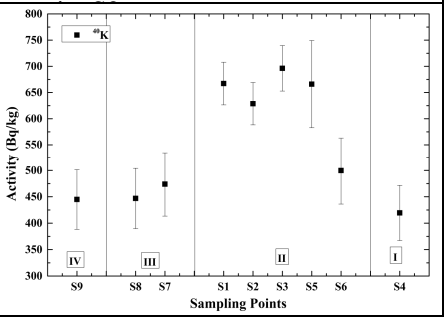
a. ^{226}Ra, ^{235}U and ^{228}Ac activity concentrations



b. Normalized activity concentrations to the reference



c. ^{210}Pb and ^{210}Pb$_{ex}$ activity concentrations



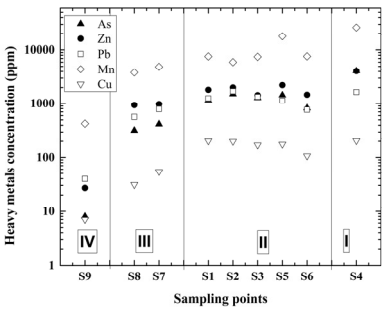
d. ^{40}K activity concentration

Figure 2: Activity concentration of the sampling sites

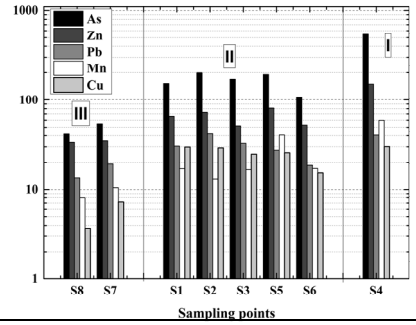
The activity concentrations of ^{226}Ra, ^{228}Ac, ^{235}U and ^{40}K were measured by means of γ-ray spectrometry and were found between (20-100) Bq/kg, (20-35) Bq/kg, (2-7) Bq/kg and (420-700) Bq/kg, respectively. The uncertainty was calculated in 1σ standard deviation and ranged from 3 to 6% for ^{226}Ra, 12 to 28% for ^{235}U and 7 to 8 % for ^{228}Ra, 6 to 7% for ^{40}K and 10 to 16% for total ^{210}Pb. The highest activity concentrations of ^{226}Ra and ^{235}U were found near the load out pier area (region I, S4) and were 4 and 2.5 times higher than those in the reference site (region IV). In the neighbouring sites (region II) radioactivity levels were measured 35-40 % and 25-35% lower for ^{226}Ra and ^{235}U, respectively and were 2 and 1.5 times higher than the values measured in Ierissos port (region IV). Near Kokkinolakkos River (region III) ^{226}Ra and ^{235}U exhibited comparable values with the reference site S9 (region IV). The activity concentrations of ^{228}Ac, they were found comparable as the one of S9, in all the sampling sites. Finally, ^{40}K radioactivity levels in the sites S 1, 2, 3, 5 were found enhanced by 40-50% of S9. On the other hand, ^{40}K radioactivity levels in the sites near Kokkinolakos River (S 7, 8), outside the pier area (S6) and the load out pier area (S4) were found similar to S9.

The activity concentration of ^{210}Pb is separated into the total activity concentration and the excess activity concentration (^{210}Pb$_{ex}$). The radionuclide ^{210}Pb in the marine sediment originates from radon ^{222}Rn that either could be supported by quantities of ^{226}Ra in the sampling location and/or by radon that is transferred in the sampling location as a result of other environmental processes (atmospheric scavenging, diffusion from deeper seabed layers etc.). So, the activity concentration in the samples is the total of both portions/origins (^{210}Pb$_{tot}$). The excess portion was calculated by subtracting the activity concentration of ^{226}Ra from the total activity of ^{210}Pb. Both total and excess activities are

depicted in Fig 3. The ratio of the ^{210}Pb excess to the total ^{210}Pb activity concentration was 25%, 50% and 60% in the load out pier area, the rest area of Stratoni port and Kokkinolakkas River estuary, respectively.



a. As, Cu, Mn, Pb, Zn concentration in all sampling sites (logarithmic scale)



b. Normalized heavy metal concentration to the reference site S9

Fig. 2 Heavy metals concentration in all sampling sites

The concentrations of the most toxic heavy metals were measured with x-ray spectrometry and were found (8-4100) ppm, (30-4000) ppm, (7-200) ppm, (40-1700) ppm and (400-26000) ppm for As, Zn, Cu, Pb and Mn, respectively The highest values were observed near the load out pier area (region I). In region I the concentration of As were 3 orders of magnitude higher, while the concentrations of Zn, Cu, Pb and Mn were 2 orders of magnitude higher than the values of the reference site (region IV). In region II the concentrations of As were more than 2 orders of magnitude higher, while the concentrations of Zn, Cu and Pb were 2 orders and concentrations of Mn were 1 order of magnitude higher than those in the reference site. However, in sampling point S5, Mn concentration was 3 orders of magnitude higher than those in Ierissos port (region IV). The mean measured values in region III (Kokkinolakkas River estuary) were 370 ppm, 960 ppm, 40 ppm, 680 ppm and 4400 ppm for As, Zn, Cu, Pb and Mn, respectively. In region III, As and Zn concentrations were 2 orders of magnitude higher, while Cu, Pb and Mn concentrations were 1 order of magnitude higher, than the concentrations of Ierissos port.

4. Conclusions/Discussion

In this work enhanced values of ^{226}Ra activity concentrations were found in Stratoni port and especially near the load out pier area, in comparison with the ones of the reference site. However, ^{232}Th activity concentrations were in good agreement, within uncertainties, for all sampling points as the one measured in the reference site (region IV, Ierissos port). Moreover, the concentrations of the studied trace metals exhibited the highest concentrations near the load out pier area (above 2 orders of magnitude higher than the reference site). The enhanced values of the trace metals, represent a potential radiological hazard, as well as a serious chemical impact on humans and the environment. Additionally, the concentrations of most trace metals were higher than previous measurements in the same region, in coastal areas of Greece, as well as in coastal areas and rivers of the Mediterranean, where anthropogenic activities were present. Furthermore, the studied trace metals (except of Cu) concentrations were well above the guidelines set by organizations of America, Australia and Ontario (USEPA, ANZECC, OMEE).

5. Acknowledgements

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