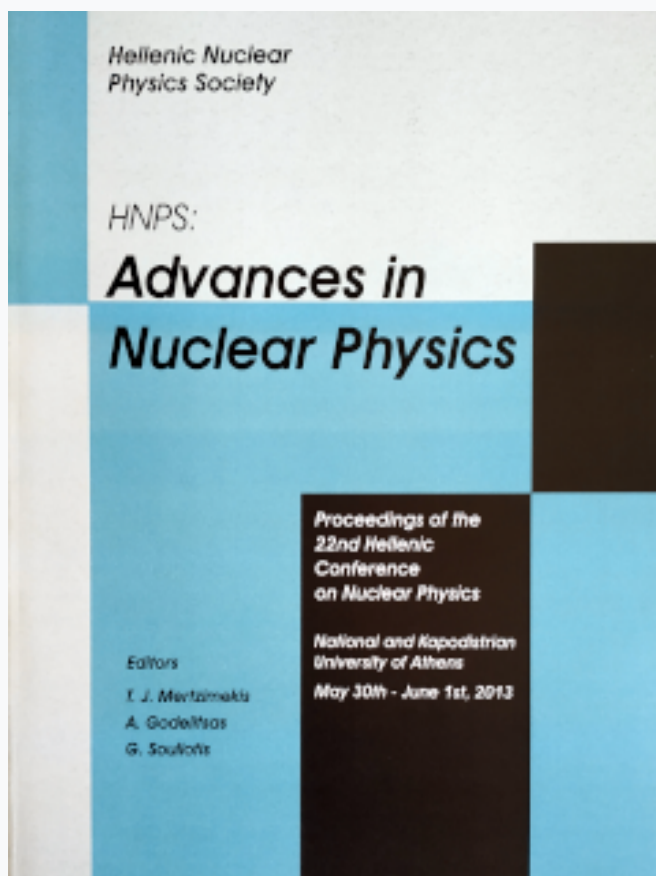


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# Sediment pollution by radionuclides and toxic metals in the Ierissos Gulf, North Aegean Sea, Greece

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## Abstract

Environmental pollution of industrial areas and especially of areas which contain industries that involve processing of NORM (Naturally Occurring Radioactive Materials), requires monitoring radionuclide activities and trace metal concentration. In the gold mine facility of Stratoni region in Ierissos Gulf, surface sediment samples were analysed regarding TENORM (Technologically Enhanced NORM) and toxic metals (e.g. As, Pb, Cu, Cr and Ni). Radionuclide activity concentrations ( $^{226}\text{Ra}$ ,  $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ,  $^{210}\text{Pb}$ ,  $^{228}\text{Ac}$ ,  $^{212}\text{Pb}$ ,  $^{212}\text{Bi}$ ,  $^{208}\text{Tl}$ ,  $^{40}\text{K}$ ) were measured by means of gamma-ray spectrometry using a high-purity germanium (HPGe) detector, while the trace metals concentrations were determined using the XRF (X-Ray Fluorescence) technique. The results indicate that the surface sediments of the Ierissos Gulf are significantly polluted with As, Pb and Cu. Surface distribution analysis of the studied radionuclides and toxic metals (e.g. TENORM, As, Pb, and Cu) indicates maximum contamination levels close to the factory area, which decrease gradually with increasing distance from the shore. The interpretation of the increased levels is under investigation since the load-out facility of the mining operations in the town of Stratoni affects the whole ecosystem.

*Keywords:* Heavy metals, Stratoni, gamma-ray spectrometry, gold mine

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## 1. Introduction

Mine processing ends up with large amounts of by-products, mainly originating during the chemical separation of the metal from the ore. Mining involves both open-cut and underground operations. The ore is crushed, panned and the remaining waste rock is dumped into heaps as tailings [1]. The residual material contains natural radionuclides that are found in the rock itself since the bearing ore is often associated with enhanced uranium concentrations [2]. Moreover, the residual material may also contain quantities of heavy metals (e.g. As) due to the process of the metal separation from the ore.

More specifically gold mining plants are active in many areas worldwide and they are considered as areas that may cause pollution due to the U bearing tailings and the heavy metals release to the environment (e.g. Pb and As) [2–4]. As and Pb are considered hazardous substances and are the dominant metals found in gold-sulfide deposits, since they are the main contained minerals in arsenopyrite (FeAsS) and galena (PbS), respectively. Under natural conditions, they are relatively stable. However, if mining processing are involved, the minerals are broken down due to the exposure to oxygen and water [3].

The research performed in areas with mining activities concerns mostly the terrestrial and not the marine environment. As far as radionuclides in seawater and sediments are concerned there is a lack in literature regarding their spatial and temporal evolution. Nevertheless, marine sediments are a major repository of heavy metals in coastal areas and their study plays an important role in the quality assessment of the marine environment. Moreover, the geochemistry of the sediments plays an important role in the study of pollution

pattern of soils. Metals prefer the sediment phase, thereby facilitating the elimination of metals from the water column thus sediments serve as sinks to metals. However, the metals can be released back to the water when changes in the environment occur, such as changes in the pH, redox potential or the presence of organic materials [4].

According to a previous study [5], surface sediment samples from Strymonikos and Ierissos Gulfs were analyzed for Cu, Pb, Zn, Cr and Ni concentrations. The sea-bottom area located at the load-out facility of the mining operations in the town of Stratoni (Ierissos Gulf) was established as the most polluted region. However, the activity levels in the marine environment in the specific area have not been reported. The coastal marine ecosystems of Strymonikos and Ierissos Gulfs (Fig. 1) are commercial fishing grounds (trawling is not allowed in the Ierissos Gulf) and are adjacent to areas of important industrial and agricultural activities [5]. Any potential pollution affects directly the human health and marine life, while, indirectly, it may cause disequilibrium to the marine species, bio-societies and food chain. In this study surface sediment samples from the mine area of Stratoni and the adjacent area have been analyzed for TENORM and toxic metals, in an attempt to study the possible impact of human activities in the area.

## 2. Study area and methodology

The Stratoni area is situated in the Chalkidiki Peninsula, northern Greece (Fig. 1). The study area lies between latitudes  $40^{\circ} 30'$  and  $40^{\circ} 32.5'$  and longitudes  $23^{\circ} 45'$  and  $23^{\circ} 32.5'$ . It is characterized by a mountainous relief with 92% of the surface covered by forest. Starting at 10 km west of Stratoni village, a P–Zn–Mn deposit is present and exploited in the Varvara Mine. Moving eastwards along the Stratoni–Varvara fault, Pb–Zn sulfide ore forms within the marble as well as along the contact between the gneiss and the lower marble horizon. Major deposits of this type have been exploited at Madem Lakkos, Olympias and Mavres Petres mines. The major minerals present in the Stratoni deposit are pyrite, arsenopyrite, galena and rhodochrosite. Copperiferous pyrite has also been extracted at Madem Lakkos during the 1970s. Another ore type of the area is the porphyric Cu–Au deposits in Skouries and Fisoka, south of Stratoni village. Major minerals present in this ore are pyrite, chalcopyrite, bornite and magnetite [6].

It should be noted here that mining activity dates back to prehistoric times and continues until today. During the last century, several mining companies exploited the sulfide and manganese ore deposits of the wider area (Madem Lakkos, Mavres Petres and Piavitsa ore bodies) extracting million of tons of mixed sulfide, manganese oxide and pyrite. Acid mine water, deriving from both Mavres Petres and Madem Lakkos mines, is directed to the water treatment plant, located next to the Stratoni flotation plant where treatment is carried out in agitated reactors with hydrated lime ( $\text{Ca}(\text{OH})_2$ ) for neutralization. Mine waste and fine grained tailings, produced by the flotation procedure, are disposed at the controlled Chevalier site, next to Stratoni village. Coarse grained tailings mixed with cement and water are commonly used for backfilling the mining shafts and adits [7].

A total of 9 surficial marine sediments (upper 2cm layer) were collected from Ierissos Gulf (STRAS 1, 2, 3, 4, 5, 6, 7, 8, 9). One sample was collected in the area of the load out pier of the mining plant (STRAS 4), five samples (STRAS 1, 2, 3, 5, 6) were collected from the neighboring sites (Stratoni region), two samples (STRAS 7, 8) near Kokkinolakkos River estuary and STRAS 9, near Ierissos region (away from Stratoni region and Kokkinolakkos River). Sample STRAS9 can be thought as being a reference sample.

The samples were processed by a standard procedure including drainage, sieving and pulverization, so as to achieve a homogeneous powder with a maximum grain size of  $63 \mu\text{m}$ . The samples remained tightly closed to their final boxes (geometry: 68 mm inner diameter and 18 mm inner height) for at least 21 days in order to achieve secular equilibrium between Radon daughters and  $^{226}\text{Ra}$ . The measurements were carried out by means of a High Purity Germanium (HPGe) detector. The spectrum analysis was performed using the SPECTRW spectroscopy software package [8].

The trace elements concentrations were determined in three sediment samples (STRAS3, 4 and 7) using the XRF technique. Only for the sample STRAS3, a grain size separation was performed prior to the XRF analysis. More specifically, two samples were prepared, with a grain size distribution ranging from  $63 \mu\text{m}$  to 2 mm grain diameter (STRAS3.2) and a second sample (STRAS3.63) which included only grains with



Figure 1: The sampling locations from Ierissos Gulf focused at Stratoni region.

diameter smaller than  $63 \mu\text{m}$ . In this way the preference of the absorption in different grain size clusters was additionally studied.

The activity concentrations (in units Bq/kg) were calculated by analyzing the gamma-ray spectra using the following 1 formula [7].

$$Activity = \frac{counts}{eff \cdot t \cdot m \cdot I_{\gamma}} \quad (1)$$

where:

$t$ : is the time measurement of each sample (24 h),

$eff$ : the absolute photopeak efficiency

$m$ : the mass (in kg) of each sediment sample

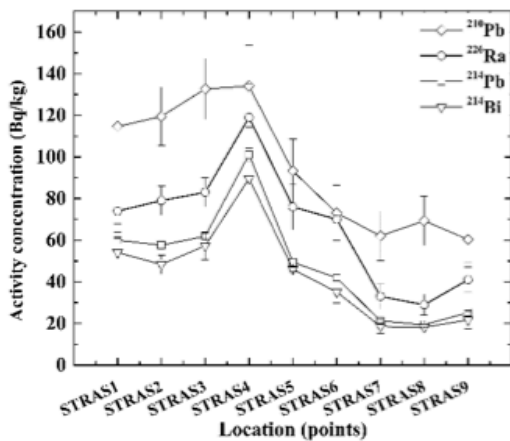
$I_{\gamma}$ : the emission probability of the gamma-ray lines of interest.

The efficiency calibration of the HPGe detector was performed using a reference  $^{152}\text{Eu}$  source. Among the analyzed photopeaks there was a case of two folded photopeaks at 185.71 keV ( $^{235}\text{U}$ ) and at 186.21 keV ( $^{226}\text{Ra}$ ). Assuming that  $^{238}\text{U}$  and  $^{226}\text{Ra}$  are in secular equilibrium and using: (a) the known relative abundance in nature of the two Uranium isotopes (99.3% for  $^{238}\text{U}$  and 0.7% for  $^{235}\text{U}$ ); and (b) the decay branching in each case, one can readily calculate the expected detected relative intensity of the two gammas (0.43 and 0.57 for the 185.71 keV and the 186.21 keV, respectively).

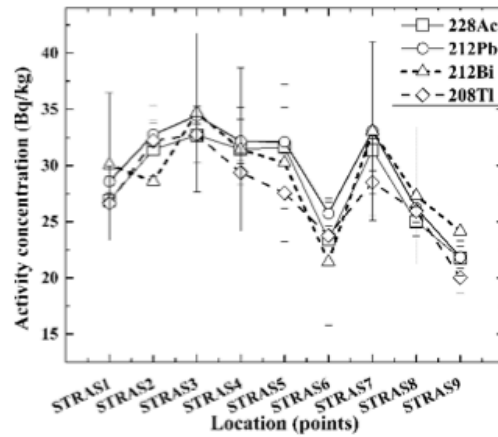
### 3. Results and discussion

The results of the activity (Bq/kg) and the trace element ( $\mu\text{g}/\text{gr}$ ) concentrations are depicted in Fig. 2.

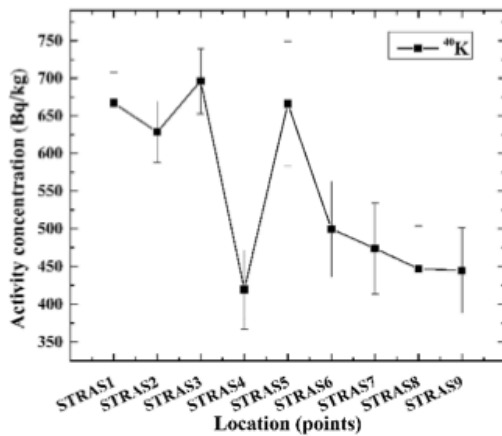
Arsenic concentrations ranged from 340 to 4094  $\mu\text{g}/\text{g}$ , Pb from 789 to 2988  $\mu\text{g}/\text{g}$  and Cu from 54 to 336  $\mu\text{g}/\text{g}$ . Enhanced activity levels were observed for the radionuclides of the  $^{238}\text{U}$  decay series. The activity of  $^{226}\text{Ra}$  was found to range between 21 and 121 Bq/kg, while the activity of the  $^{222}\text{Rn}$  daughters ( $^{214}\text{Pb}$ ,  $^{214}\text{Bi}$ ) from 20 to 101 Bq/kg. Furthermore, concerning the  $^{232}\text{Th}$  series, the activity of  $^{228}\text{Ac}$  varied from 21 to 35 Bq/kg, while the  $^{220}\text{Rn}$  daughters ( $^{212}\text{Pb}$ ,  $^{212}\text{Bi}$ ,  $^{208}\text{Tl}$ ) from 22 to 35 Bq/kg. As concerns  $^{40}\text{K}$  and  $^{210}\text{Pb}$ , their activities varied from 423 to 634 Bq/kg and from 57 to 126 Bq/kg, respectively.



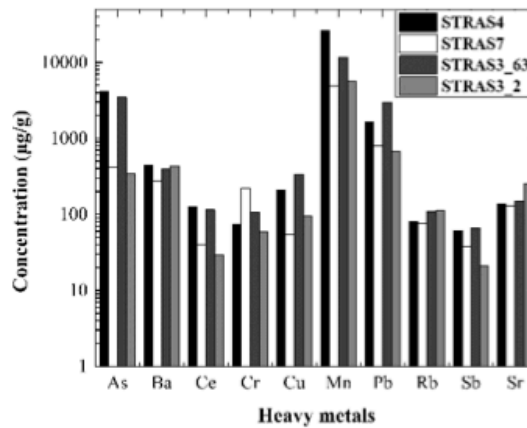
a.) The  $^{238}\text{U}$  series



b.) The  $^{232}\text{Th}$  series



c.) The radionuclide  $^{40}\text{K}$



d.) Trace element (As, Ba, Ce, Cr, Cu, Mn, Pb, Rb, Sb and Sr) concentrations

Figure 2: The activity and trace metal concentrations for all the measured sediment samples.

The activity levels of the  $^{238}\text{U}$  daughters were found to be enhanced mainly in the area of the load out pier of the mining plant (STRAS4), while the observed activity levels in the neighboring sites (STRAS 1, 2, 3, 5, 6) were 35-40% lower.

Enhanced concentrations of Pb, As, Mn and Cu were also found in the area of the load out pier of the mining plant (STRAS4). Off the pier area (STRAS7) the same elements exhibited much lower concentrations (decreased by one order of magnitude). The results (except for As and Mn) are comparable with recent corresponding measurements in the local water streams sediments [7] indicating weathering / transportation via the streams that flow into the gulf. The As and Mn concentration values in the marine sediments were found higher compared to the values reported in the literature [9] especially in the sites close to the load out pier area (STRAS3, 4).

#### 4. Conclusions

In this work, the preliminary results of the trace metals and the radionuclide concentrations were presented. Further analysis to determine the grain size distribution and the mineralogy in the collected sediment samples will be performed.

According to this work the need of systematic monitoring programs throughout the coastal line was emphasized and especially near coastal areas of intense anthropogenic activities (industries, agriculture, aquaculture, mining etc.).

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I would like to express my gratitude to Dr. C.K. Kalfas for providing the SPECTRW spectrometry software package and his continuous help. This work was supported by GSRT (Hellenic General Secretariat for Research and Technology) in the frame of the project "RADIOSCOPIO: Research and development of an in-situ underwater gamma-ray spectrometer for low-level radioactivity measurements" under Greece-China Bilateral R&TD Cooperation 2012-2014.

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