

## Spatial and temporal NORM studies in coastal areas of Greece near polymetallic mines

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### Abstract

Spatial and temporal NORM studies have been held in two coastal areas of Greece, near an **active polymetallic** mine and an **abandoned** one. The metal exploitation resulted in **enhanced** concentrations of natural radioactivity and especially  $^{226}\text{Ra}$  and  $^{235}\text{U}$  in the marine sediment. Thus, the dispersion of the aforementioned radionuclides was estimated via ERICA Assessment Tool (Brown et al., 2016) and revealed an **affected marine area** of **21 Km<sup>2</sup>**. Additionally, the radiological risk was assessed for marine biota utilizing ERICA, however the **risk** was found to be **negligible**. The temporal study was based on the radio-tracing techniques of  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ , which were applied in sediment cores and resulted in the reconstruction of the anthropogenic impact of the last 150 years. The vertical profiles of **radionuclides** (e.g.  $^{226}\text{Ra}$ ) were **combined** with **metal** concentrations to verify the history of the anthropogenic activity. The risk assessment for metals (both spatial and temporal) was determined by pollution indices and revealed extreme enrichment of metals in the sediments for both study areas.

### Results and Discussion

The measured activity concentrations of  $^{226}\text{Ra}$  and  $^{40}\text{K}$  in **Stratoni** in Fig. 2A exhibited an increase by 24% and 26%, respectively, from the surface to the deeper layers. The  $^{232}\text{Th}$  values were constant along with depth. The results reflect the discharge of mining wastes in the coastal area of Stratoni, as these wastes are rich in  $^{226}\text{Ra}$  and possibly  $^{40}\text{K}$  but not in  $^{232}\text{Th}$ . It is evident that the discharge occurred constantly till 1980, after which a decrease is observed. Different scenarios can be considered to justify this trend, either recent deposition was enriched with **low concentration** of NORMs or the **disposed activities were stopped** (Pappa et al., 2019a).

In Oxygono Bay core in Lavrio) the  $^{226}\text{Ra}$  and  $^{232}\text{Th}$  values increased progressively in the period of 1860 - 1915 and remained almost constant after 1915, while  $^{40}\text{K}$  activity concentrations decreased gradually in the periods 1860 - 1915, 1915 - 1965 and 1965 - 2014 (Fig. 2B). Despite the fact that the activity concentrations of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$  were low, compared to Stratoni (Fig. 2A), the observed variations in their profiles are **connected with the mining activities** in the area (Pappa et al., 2018).

In both studied areas the **metal concentration profiles** (e.g. As, Cu, Pb, Zn) and **spatial distributions** were similar with  $^{226}\text{Ra}$ . Additionally, the risk assessment for metals (both spatial and temporal) was determined by pollution indices and revealed **extreme enrichment of metals** in the sediments for both study areas.. however are not presented here for reasons of brevity.

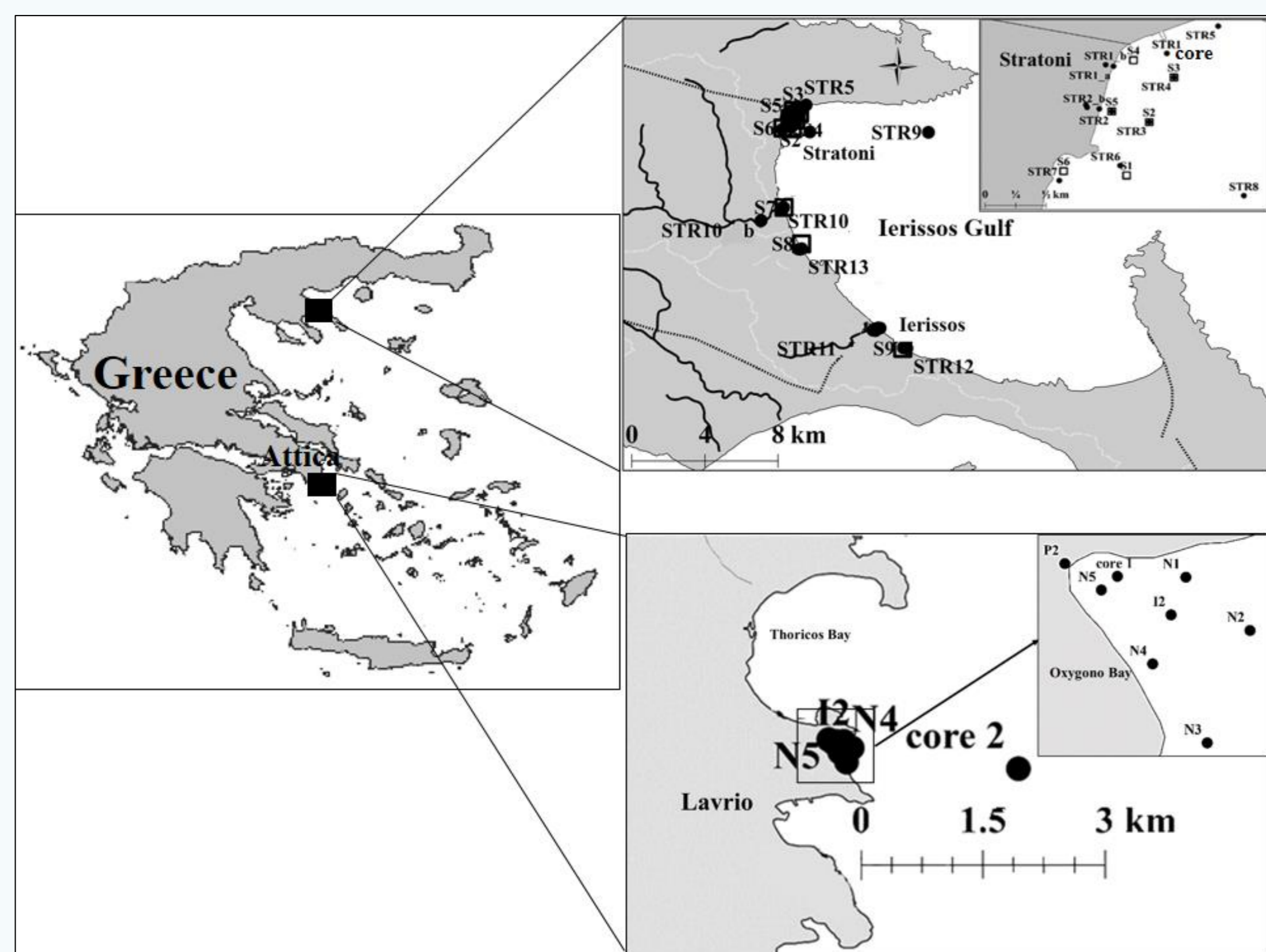


Figure 1. The map of the study areas in Greece, where the surficial sediments and the sediment cores were collected.

### Introduction

Mines are usually situated in the vicinity of rivers, lakes or coastal areas. Specifically, the latter acts as a receptor for both water transfer contaminants (river and drainage basin routes) and/or direct waste disposal. In this work two coastal areas of Greece, **Stratoni** and **Lavrio**, were studied, where similar mining activities due to exploitation of similar type minerals are **still occurring** and have **ceased**, respectively. The mining history in both areas begins from ancient times and lasts until nowadays.

### Methodology

In this work the **activity concentrations** (in Bq Kg<sup>-1</sup>) in **surficial sediments** and **sediment cores** of  $^{226}\text{Ra}$  ( $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ ),  $^{232}\text{Th}$  ( $^{228}\text{Ac}$ ) and  $^{40}\text{K}$ , were determined via gamma-ray spectrometry and were used as a tracer for the mining activities. The activity concentrations were studied in a temporal manner (along with time). The temporal study was applied in the sediment cores using radiochronology (based on natural ( $^{210}\text{Pb}$ ) and artificial ( $^{137}\text{Cs}$ ) radionuclides) and was verified by metal historical data, which are not presented in this work for reasons of brevity.

Additionally, the obtained activity concentrations per core slice (1 or 2 cm) were combined with the ERICA parameters and the radio-dating techniques to estimate the total dose rates for the last 100 years. For all the inserted parameters default values were used except for the CR and Kd parameters. In this case, default and, when possible, experimentally determined user defined values were utilized for the radionuclides of interest. Moreover, the generic transfer model of ERICA was utilized to estimate the activity concentrations of the observed TENORMs.

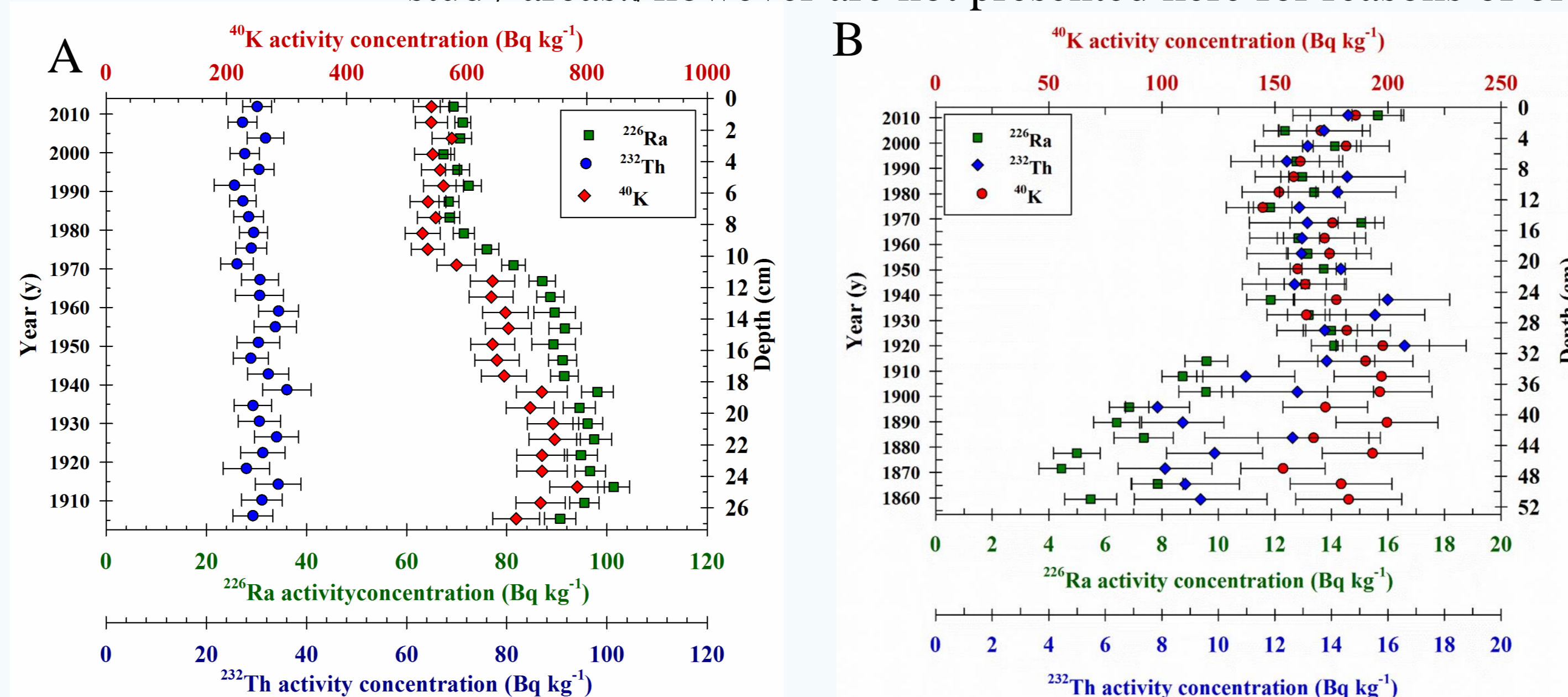


Figure 2. The radionuclide profiles at A) Stratoni (A) and Lavrio (Oxygono Bay) (B) of  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$  and  $^{40}\text{K}$ . The  $^{232}\text{Th}$  profile was produced by  $^{228}\text{Ra}$  profile assuming approximate equilibrium with  $^{228}\text{Ra}$  and  $^{228}\text{Ac}$ , as the presence of  $^{228}\text{Ra}$  ( $t_{1/2}=5.8$  y) and  $^{228}\text{Ac}$  ( $t_{1/2}=615$  h) in the environment can be only due to the very long half-life of their parent nuclide..

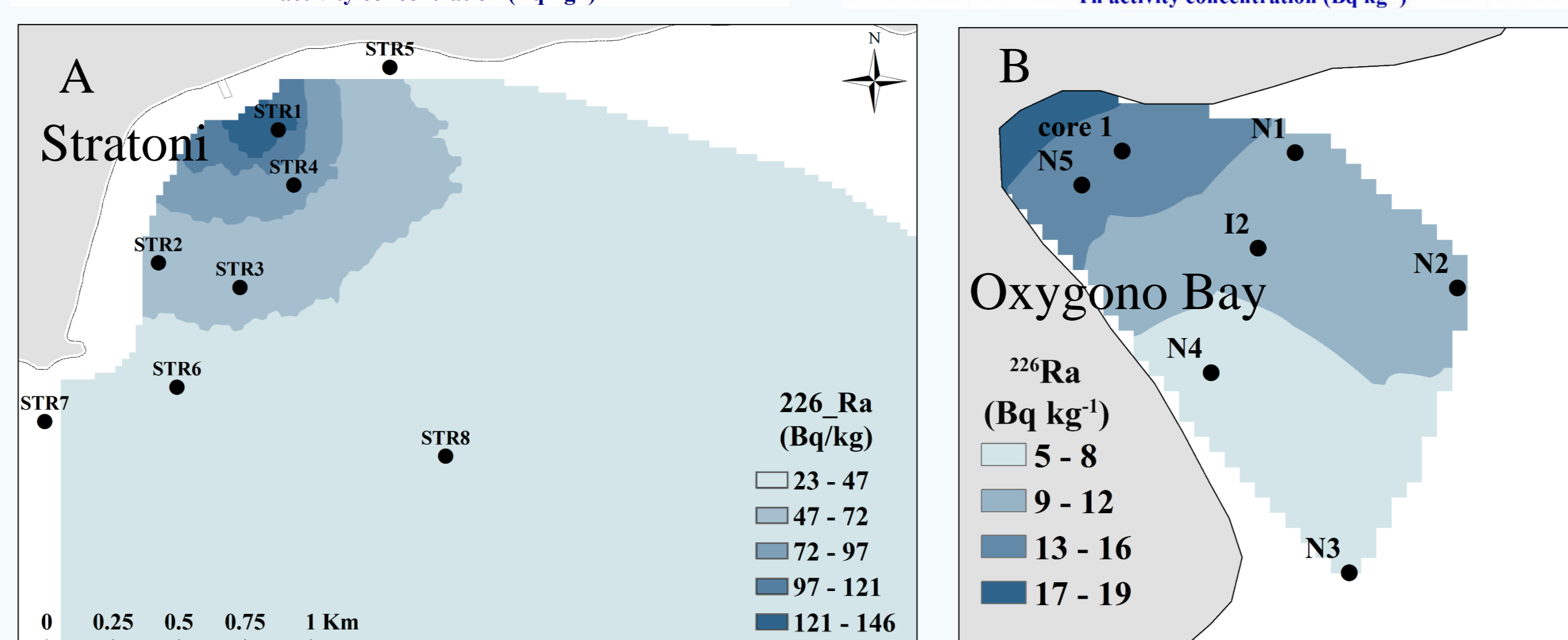


Figure 3. The estimated activity concentrations based on the generic transfer model of ERICA software for Ierissos Gulf (Stratoni) are presented in Fig. 3A. In Oxygono Bay (Lavrio) due to the low number of surficial samples, it was used a geostatistical model (Kriging) for the spatial activity concentration determination.

The surficial data both in Ierissos Gulf and in Lavrio revealed that  $^{232}\text{Th}$  activity concentrations were unaffected by the anthropogenic activities (similar concentrations among the sampling sites). Small variations of  $^{40}\text{K}$  concentrations were attributed to geological factors. It should be noted that in both areas the activity concentrations of  $^{226}\text{Ra}$  and  $^{235}\text{U}$  varied greatly among the studied sites where the highest values were found near the floatation plant of Stratoni and the waste disposal site of Oxygono. Thus, **technically enhanced NORMs** were observed in the marine area of the studied polymetallic mines and where **strongly connected** with the mining activities. Additionally, in Ierissos Gulf the spatial data were used to estimate the **affected area** (Fig. 3A) due to mining and was found to be **21 Km<sup>2</sup>** (Pappa et al., 2019b). A geostatistical study was also performed in Oxygono Bay (Fig. 3B), due to the low number of samples and the area with the highest concentrations was near the beach. To **assess the radiological risk** the ERICA Tool was utilized and the estimated dose rates were found **well below** the proposed screening levels by ERICA.

### Conclusions

Radio-dating techniques were applied to study the **historical archives** of mining activities in Stratoni and Lavrio, Greece which produced low technically enhanced NORM variations. Additionally, spatial NORM distribution studies were used to verify the site with the highest radionuclide activity concentrations and estimate the affected marine area due to mining (**21 Km<sup>2</sup>** in Ierissos Gulf, Stratoni). The radiological risk was found **negligible** for the last **100 years** for both areas, however the metal risk was extremely high.

### Acknowledgements

The authors acknowledge the local authorities and corresponding communities in Ierissos and Lavrio cities for supporting the sampling campaigns and for providing facilities to implement the experimental work in the coastal areas

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