

## HNPS Advances in Nuclear Physics

Vol 21 (2013)

HNPS2013



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doi: [10.12681/hnps.2023](https://doi.org/10.12681/hnps.2023)

#### To cite this article:

Eleftheriou, G., Tsabaris, C., Kapsimalis, V., Patiris, D. L., Androulakaki, E. G., Pappa, F. K., Kokkoris, M., & Vlastou, R. (2019). Radionuclides and Heavy Metals Concentrations at the Seabed of NW Piraeus, Greece. *HNPS Advances in Nuclear Physics*, 21, 156–159. <https://doi.org/10.12681/hnps.2023>

# Radionuclides and Heavy Metals Concentrations at the Seabed of NW Piraeus, Greece

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## Abstract

The coastal area of Piraeus is an environmentally aggravated region since many decades due to persistent pollution sources as the international port of Piraeus, a coastal fertilizers plant, the Athens sewage outfall and the industrial zone of Eleusis Bay. Recent sediment samples from the seabed of NW Salamina strait (upper Saronikos Gulf) were collected and analyzed for radionuclides and heavy metals composition. Measurements of 22 samples were performed including granulometrical analyses using wet sieving treatment, radiological measurements using high resolution gamma-ray spectrometry and determination of main heavy metals concentrations using the XRF technique. The activity concentrations of all radionuclides exhibited values expected in natural sediments, while the heavy metals concentrations are locally far above the sediment quality guidelines values. The most contaminated area is the small harbor of the ex fertilizers plant at Sfageion Bay, where discrepancy from the linear correlation between the unsupported  $^{210}\text{Pb}$  with the trace Pb is indicative of the prior intensive pollution. The measured activity concentrations of  $^{137}\text{Cs}$  combined with these of naturally occurring radionuclides were also used to estimate the sedimentological texture of the studied region.

**Keywords:** sediment, radionuclides, heavy metals, seabed, Piraeus port

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## 1. Introduction

The coastal area of Piraeus is an environmentally aggravated region since many decades due to persistent pollution. The main sources of this pollution are: (a) the international port of Piraeus with one of the higher traffic in the Mediterranean Sea, (b) the Athens sewage outfall discharging untreated domestic and industrial wastewater direct into the swallow water for more than 20 years (until 1994), (c) the industrial zone of Eleusis Bay including more than 30 industries including petroleum refineries, shipyards, steel works, foundries, chemical, electrochemical and cement factories, all of which are known to have heavy metal discharges and (d) a large fertilizers factory working until the end of 90'.

Various studies have confirmed the contamination of the region by heavy metals, toxic elements and organic components. However, limited are the measurements concerning the radionuclides concentrations in the sea water and even less for the activity concentrations at the sediment [1]. In this work, recent sediment samples from the seabed of NW Salamina strait (upper Saronikos Gulf) have been collected and analyzed for radionuclides and heavy metals composition, in order to provide updated values of the contamination levels and a radiological profile baseline.

## 2. Materials and Methods

### *Study Area*

The study area is the strait connecting the Gulfs of Saronikos and Eleusis, at the North Western cost of Piraeus port (Keratsini Bay) covering an area of approximately 22 km<sup>2</sup> (Fig. 1). The mean depth is 11 m

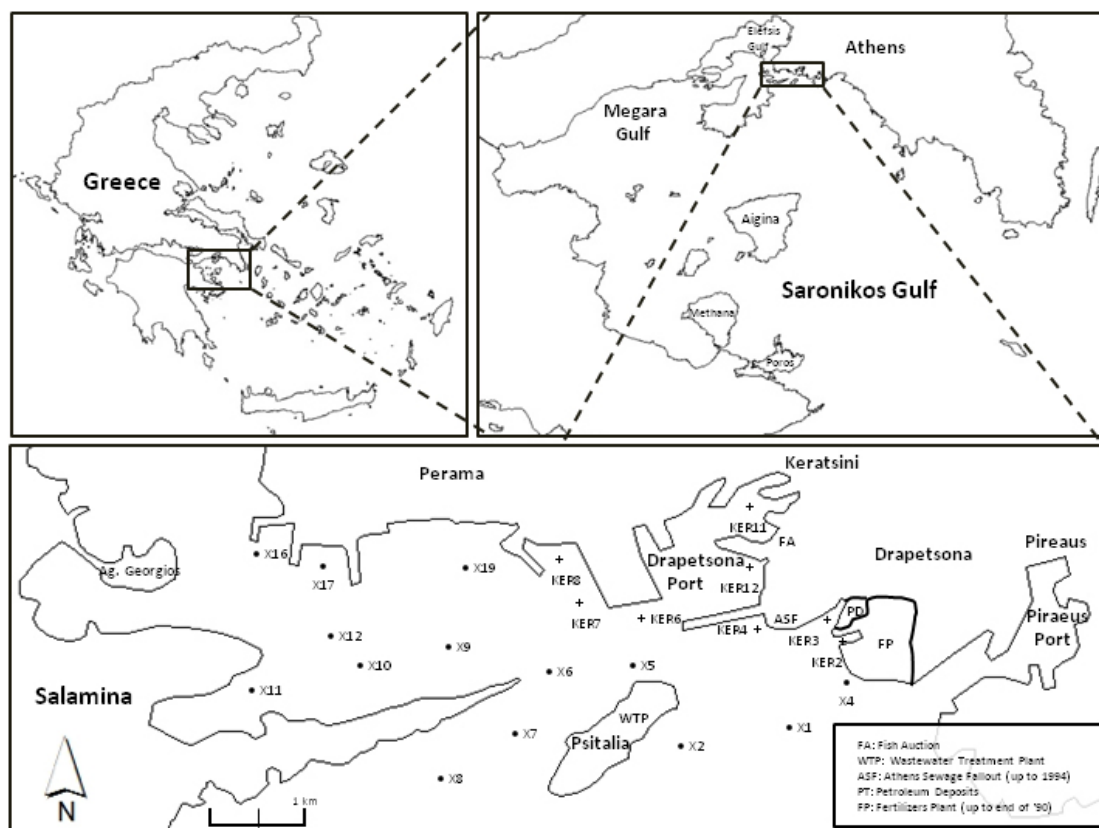


Figure 1: Sediment sampling positions at NE Elefsis strait, upper Saronikos Gulf

throughout the strait. Two sampling surveys took place at Keratsini - Drapetsona Bay and Perama Channel coastal region at 28/12/2011 and 24/2/2012, respectively. In total 22 seabed surface sediment samples were collected for analysis.

### Methodology

The collected samples were properly treated and measured at the HCMR laboratories. The measurements included granulometrical analyses with wet sieving treatment, radiological measurements using high resolution spectrometry (with a 50% HPGe detector) and determination of main heavy metals concentrations using XRF technique.

## 3. Results and Discussion

### Concentrations

The radionuclides activity concentrations varied from 2.3 to 64.1 Bq/kg for  $^{226}\text{Ra}$  (as derived from  $^{214}\text{Pb}$  and  $^{214}\text{Bi}$ ), from 5.2 to 22.9 Bq/kg for  $^{232}\text{Th}$  radioactive series (mean value of  $^{228}\text{Ac}$ ,  $^{212}\text{Pb}$  and  $^{208}\text{Tl}$ ), from 0.3 to 6.6 Bq/kg for  $^{235}\text{U}$ , from 61.8 to 377.3 Bq/kg for  $^{40}\text{K}$  and from 0.3 to 6.6 for Bq/kg  $^{137}\text{Cs}$ . The concentrations of the measured heavy metals varied from 14 to 2677  $\mu\text{g g}^{-1}$  for As, from 90 to 517  $\mu\text{g g}^{-1}$  for Cr, from 42 to 567  $\mu\text{g g}^{-1}$  for Cu, from 100 to 1477  $\mu\text{g g}^{-1}$  for Mn, from 123 to 4821  $\mu\text{g g}^{-1}$  for Zn and from 47 to 1394  $\mu\text{g g}^{-1}$  for Pb. The activity concentrations of all radionuclides exhibited values expected in natural sediments [3], while the heavy metal concentrations are locally far above the sediment quality guidelines values [4].

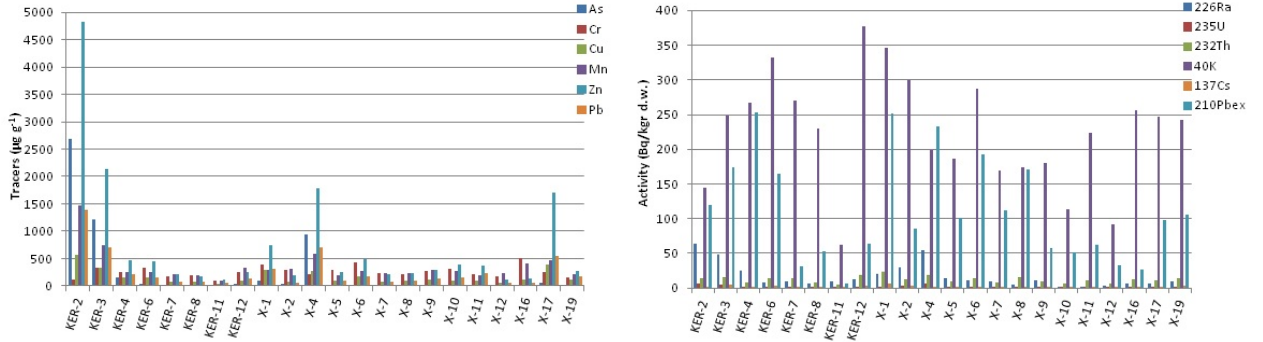


Figure 2: Main heavy metals concentrations (*left*) and radionuclides activities (*right*) at the sampling points

### Correlations

The most contaminated area is located in the small harbor of the ex fertilizers plant (Sfageion Bay), where discrepancy from the linear correlation between the unsupported  $^{210}\text{Pb}$  with the trace Pb is indicative of the prior intensive pollution. The lower  $^{210}\text{Pb}$  values can be attributed to the direct outflow of untreated sewage to the sea until 1979 (arsenipyrite and phosphate gypsum debris), explain the unexpected lower values of  $^{210}\text{Pb}$  ( $\tau_{1/2} = 22.3$  y). The proportionality between  $^{232}\text{Th}$  and  $^{40}\text{K}$  activity concentrations is indicative of the insoluble nature of Th element in sea water, while no significant correlation was obtained between  $^{238}\text{U}$  and  $^{232}\text{Th}$  or  $^{40}\text{K}$ , throughout the study region.

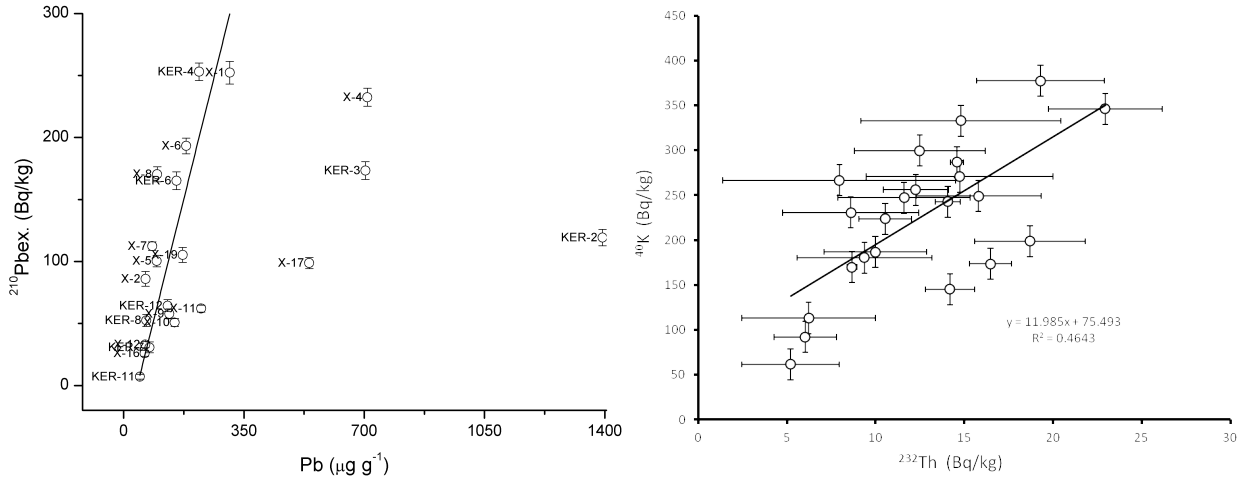


Figure 3: Correlations between (*left*) particulate Pb versus the excess  $^{210}\text{Pb}$  and (*right*) the activity concentration of natural  $^{40}\text{K}$  versus  $^{232}\text{Th}$ . The lines represent linear fit (omitting samples KER-2,3 and X-4, 17 in the first figure).

### Dose rate

The measured activity concentrations of  $^{238}\text{U}$  (as derived from  $^{226}\text{Ra}$  assuming secular equilibrium),  $^{232}\text{Th}$  (as deduced from  $^{228}\text{Ac}$ ,  $^{212}\text{Pb}$  and  $^{208}\text{Tl}$  mean value assuming secular equilibrium) and  $^{40}\text{K}$  are converted into total dose rate  $D$  using the equation:

$$D(\text{nG/h}) = 0.462 \cdot A_U + 0.604 \cdot A_{Th} + 0.0417 \cdot A_K \quad (1)$$

The absorbed dose rate varied from 9 to 45 nGy/h in the studied region; while the average dose rates in different countries ranged from 24 to 160 nGy/h and the population weighted average dose is 57 nGy/h [3].

#### Radiometric texture characterization

The textural type of the seabed was indirectly determined by the empirical factor  $F$ , i.e. the relative proportions of mud or sand fraction in sediments [2], via the expression that combines the measured activities of the  $^{226}\text{Ra}$ ,  $^{232}\text{Th}$ ,  $^{137}\text{Cs}$  and  $^{40}\text{K}$ :

$$F = -0.048 \cdot A_{Ra} + 0.24 \cdot A_{Th} + 0.65 \cdot A_{Cs} - 0.002 \cdot A_K - 3.6 \quad (2)$$

Positive values of  $F$  correspond to mud sediments (mud fraction >80%), while values lower than 1.5 designate sand and muddy sand sediments (sand fraction >50%). Values of  $F$  varying from 0 to 1.5 indicate sandy mud (mud fraction ranges between 50% and 80%).

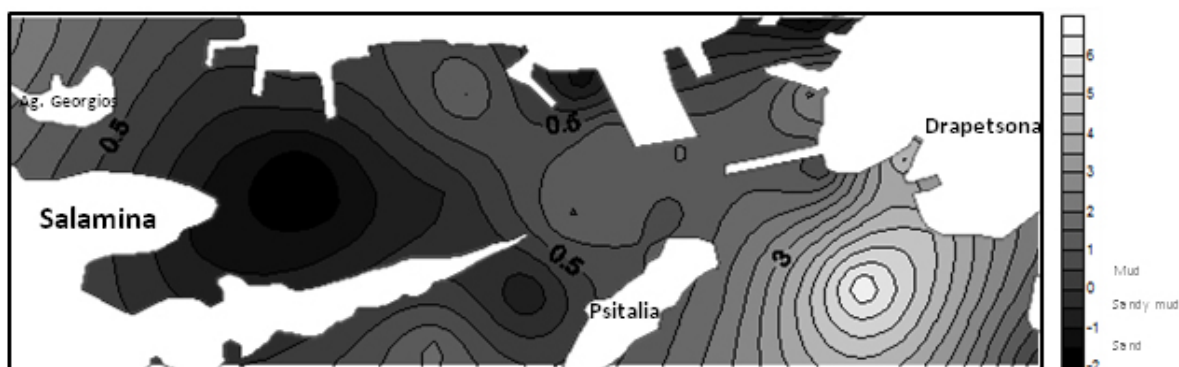


Figure 4: Textural  $F$ -factor mapping by applying Ordinary Kriging interpolation method

#### 4. Conclusion

Resent information of the main radionuclides and heavy metal concentrations in the seabed of NW Piraeus region is provided. According the tracers measurements extended contamination is observed as expected, while the radionuclides are in the natural background levels providing a baseline for future long-term monitoring studies.

#### Acknowledgments

The authors would like to thank the researcher Dr. C.K. Kalfa of the Institute of Nuclear and Particle Physics of NSCR “Demokritos” for providing us the spectral analysis programme SPECTRW and his constant help with our questions.

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