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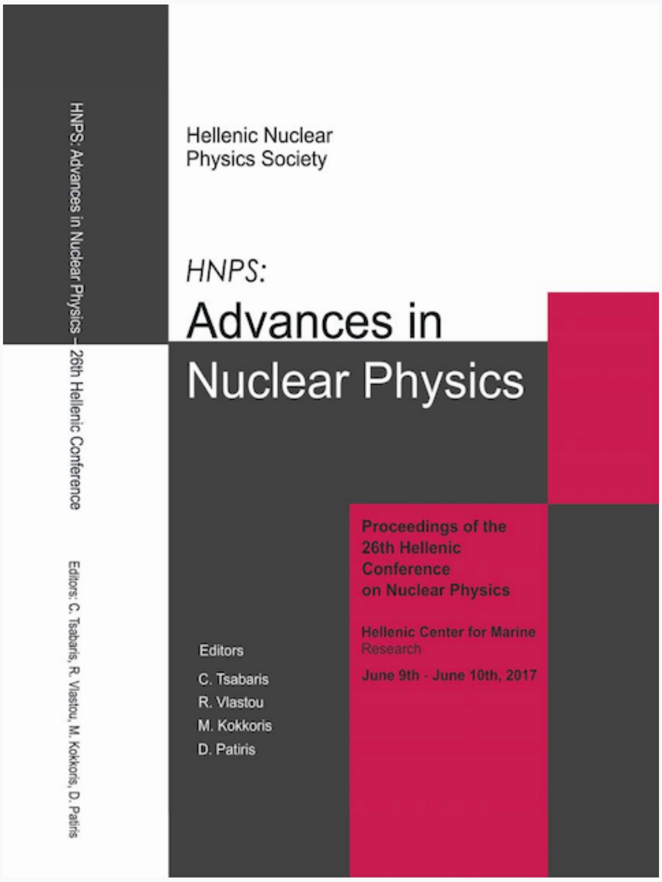

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Chronological records of metal contamination in an abandoned mine (Lavrio, Greece) using sediment profiles

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Abstract A sediment core was collected near an abandoned mine in the marine environment of Oxygono Coast at Lavreotiki peninsula to determine temporal variations among radionuclides and minor/major elements. Lavreotiki is an area where intense mining and metallurgical activities took place, from ancient until recent times. The natural radionuclide concentrations (e.g. 226Ra) were measured using gamma-ray spectrometry, while the major (e.g. Al, Ca) and minor elemental (e.g. As, Zn, Pb) concentrations were measured via X-ray fluorescence spectrometry. Additionally, the average sedimentation rates of the area were derived from the concentrations of 210Pb and 137Cs, in order to reconstruct the history of anthropogenic influence in the area. The enrichment factors (EFs) of heavy metals were determined, so in order to assess the anthropogenic influence.

Keywords Lavrio, radionuclide profile, heavy metal profiles, sedimentation rate

INTRODUCTION

Sediment profiles are commonly used in literature for the assessment of accumulation and metal pollution, the description of past environmental conditions and the investigation of history contamination at different areas [1]. The studies of heavy metal and radionuclide concentrations in sediment cores are plenty, however there are very few well-documented ones in the marine environment near mining areas. In the present work, an abandoned mining area in Lavrio has been investigated.

In general, Lavreotiki is located at the southeast of Attica, Greece and is an area where intense mining and metallurgical activities took place, from ancient until recent times. Three distinct types of wastes and tailings with different chemical and mineralogical composition can be identified in Lavrion: mining wastes, mineral processing tailings and metallurgical slags [2]. In the preliminary survey at Lavreotiki peninsula in 2014 [3], high contamination levels of trace elements and low to medium radionuclide levels were observed at the coastal zone of Oxygono beach. Therefore, a sediment core was selected in the Oxygono coast, so as to estimate the influence in the area due to anthropogenic activities in the previous years and to reveal possible associations among trace/major elements and natural radionuclides.

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EXPERIMENTAL DETAILS

Study area and field work

Three months after the preliminary survey of 2014 [3] a sediment core about 50cm depth was selected at Oxygono coast by a diver (Fig. 1).

Fig. 1. The map of the study area

Sample preparation and Experimental set-up

The sediment sample preparation is described in details in [4]. Prior to gamma-ray and X-rays fluorescence spectrometry, the core sediment samples were cleaned from stones, shells, algae and grains greater than 2 mm and were drained, sieved and pulverized, in order to achieve a homogeneous powder [5][6]. Powdered samples of 80 gr, 5 gr and 0.6 gr were used for the measurements of radionuclides, trace and major elements.

Gamma-ray spectra were obtained by means of a High Purity Germanium detector (HPGe), with nominal relative efficiency of 50% at the Nuclear Laboratory of Physics Department of National Technical University of Athens (NTUA) (Canberra GC5021). The determination of ^{210}Pb activity concentration was realized using a Ge planar detector (GL 2020R) at the Department of Physics of the Aristotle University of Thessaloniki. The cylindrical containers of the samples were placed on the detector's window, while both detectors were surrounded by a lead shield to reduce the ambient gamma-ray background. The spectrum analysis was performed using the SPECTRW spectroscopy software package [8]. All the observed photopeaks of natural gamma-ray emitters and ^{137}Cs were analysed. The efficiency calibration of the detectors, the analysis of the photopeaks and the corrections in the analysis (True Coincidence Summing effects, self-attenuation) are described in [4][9][10]. The statistical uncertainty of the photopeak counts, the intensity of the gamma-rays, the detection system efficiency and the mass were included in the uncertainty budget calculation.

The trace and major metal measurements in the sediments by means of X-ray Fluorescence is described in [4][7]. The determination of trace and major concentration was realized by a Wavelength Dispersive X-Ray Fluorescence system WDXRF. The element identification and quantification were automatically determined using the Panalytical Pro-

Trace software. Periodically the XRF system stability determination and re-calibration, was checked and achieved using reference samples. The limit of determination and the quality of the XRF method are described in [7].

Sedimentation models

The sedimentation rate (SR) was estimated using the vertical profiles of natural radionuclide ^{210}Pb and the artificial radionuclide ^{137}Cs according to [11]. The activity concentration of ^{210}Pb can be separated into the total activity concentration and the excess activity concentration. The radionuclide ^{210}Pb in the marine sediment originates from ^{222}Rn gas, which either could be supported by quantities of ^{226}Ra in the sampling location or by ^{222}Rn that is transferred in the sampling location due to other environmental processes. Therefore, the excess (unsupported) portion ($^{210}Pb_{ex}$) was calculated by subtracting the activity concentration of ^{226}Ra from the total activity of ^{210}Pb so as to remove the supported portion. According to constant flux-constant sedimentation (CF-CS) model, the excess ^{210}Pb profile was used for the SR estimation, using the equation:

$$\ln\left(\frac{A_0}{A}\right) = \frac{k}{SR} z \qquad \text{(Eq. 2)}$$

where, A_0 is the unsupported activity concentration in the sediment surface (Bq kg^{-1}), A is the unsupported activity concentration in the sediment core (Bq kg^{-1}), k is the ^{210}Pb radioactive decay constant (0.03114 y^{-1}), z is the depth (cm) and SR the mean sedimentation rate of the core (cm y^{-1}).

The ^{137}Cs peaks due to nuclear tests (1963) and Chernobyl accident (1986), allowed the estimation of the mean sedimentation rate according to the equation:

$$SR=\frac{d_i}{(t-i)} \qquad \text{(Eq. 1)}$$

where, t is the year of the sediment core collection, d_i is the depth of the ^{137}Cs peaks due to nuclear incidents (i= 1963, 1986).

Enrichment Factor (EF)

In order to estimate any potential impact due to anthropogenic activities on marine sediments the enrichment factor (EF) was calculated for each metal concentrations above an uncontaminated background level [12] (Eq. 3). The EF is obtained from the ratio of the normalized metal concentration (the concentration of the metal over a normalizer element) of the study area to that obtained at a reference area. In this work, the shale of the continental crust was used as reference area and Al as the normalizer element. According to [13], EF<1 indicates no enrichment, EF<3 corresponds to minor enrichment, EF=3–5 to moderate enrichment, EF=5–10 to moderately severe enrichment, EF=10–25 to severe enrichment, EF=25–50 to very severe enrichment, and EF>50 to extremely severe enrichment.

$$EF = \frac{\frac{M_{sample}}{Al_{sample}}}{\frac{M_{ref.}}{Al_{ref.}}} \qquad \text{(Eq. 3)}$$

where, M_{sample}, is the concentration of the metal of interest, Al_{sample} is the normalizer metal concentration, $M_{ref.}$ is the metal concentration in the reference sample and $Al_{ref.}$ is the normalizer metal concentration in the reference sample.

RESULTS AND DISCUSSION

Sedimentation rates

The vertical profiles of ^{210}Pb and ^{137}Cs are depicted in Figs 2a and 3a, respectively. The sedimentation rate obtained by ^{210}Pb (Fig. 2b) and ^{137}Cs (Fig. 3b) was 0.27 ± 0.03 cm y^{-1} and 0.23 ± 0.01 cm y^{-1}, respectively. The mean sedimentation rate (0.25 ± 0.03 cm y^{-1}) was used to reconstruct the historical levels of metals and radionuclides at Oxygono coast.

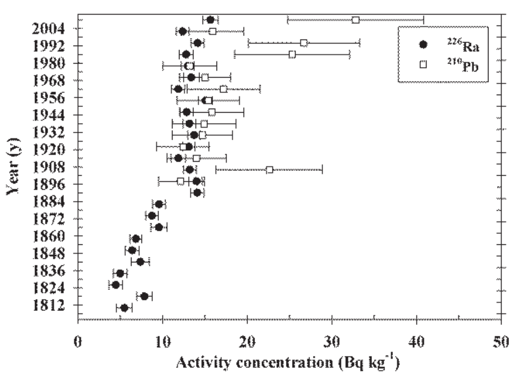

Fig. 2a. The vertical profiles of total ^{210}Pb ($^{210}Pb_{tot}$) and ^{226}Ra.

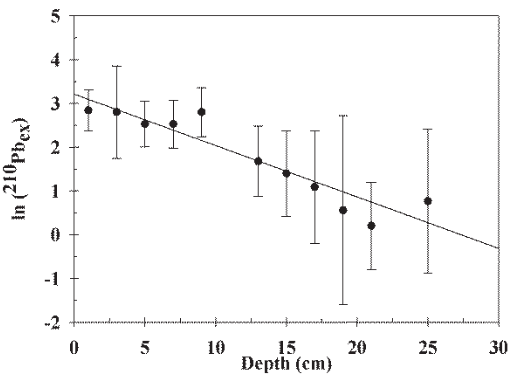

Fig. 2b. The logarithm of excess ^{210}Pb ($^{210}Pb_{ex}$) profile along with depth.

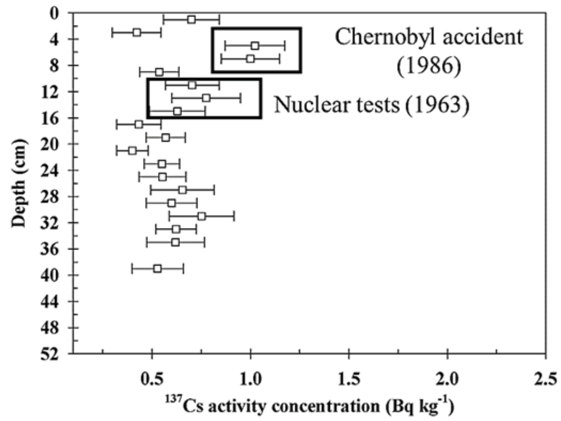

Fig. 3a. The vertical profile of total ^{137}Cs, where the nuclear incidents are mentioned.

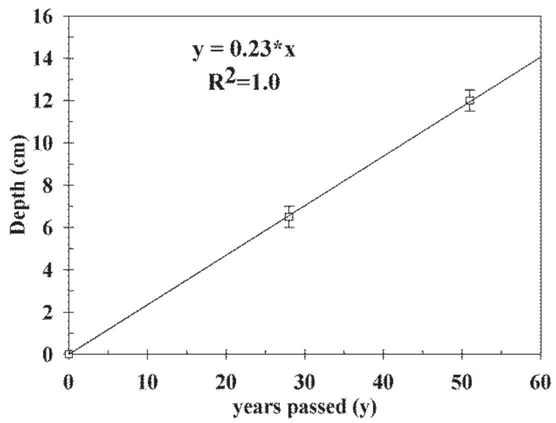

Fig. 3b. The linear association of the depth where the ^{137}Cs peaks were observed with the time passed from these incidents until the core collection.

Oxygono coast results

The activity concentration of ^{226}Ra, the concentrations of Zn (trace element) and Al (major element) are depicted in Fig. 4. Their uncertainties were 9%, 9%, 5%, respectively and their values ranged among 4-17 Bq kg^{-1}, (3.4-9.0)·10^{3} μg g^{-1} and (14-23)·10^{3} μg g^{-1}, respectively. According to the radionuclide profile the sediment core can be divided into three parts, an upper part (0-32 cm), a middle part (34-42 cm) and a lower one (44-52 cm), where the concentrations of ^{226}Ra, Zn and Al at the upper part were up to 3 times higher than those of the lower part of the core.

The observed variations in the concentration profiles represent the anthropogenic influence in the area due to mining. The lowest values of ^{226}Ra, Zn and Al were observed from 1812 to 1860 (44-52 cm) and may be indicative of the remaining slag's influence in the area. The slags were the waste products of the ancient mining (Ag, Pb) and metallurgical processes occurred in the area. From 1860 until 1900 the ancient slag exploitation occurred in the area, as the increasing values of ^{226}Ra, Zn and Al (34-42 cm) point out. From 1904 until 1989 (0-32 cm) the stability of the exploitation company lead to the exploitation of Pb (1905-1929) and Pb-Ag using Zn (1930-1989), as it is revealed by the stable values of ^{226}Ra, Zn and Al and the higher values of Zn by 13% during 1930-1989 comparing with those obtained in 1905-1929. In the early 1990's the mining operation in the area ended.

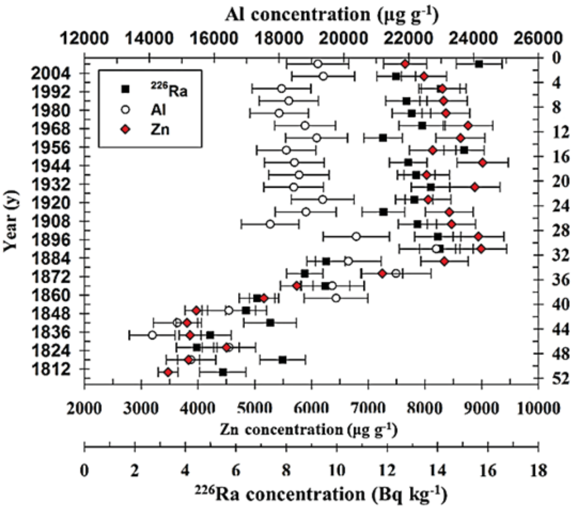

Fig. 4. Characteristic core profiles of ^{226}Ra, Al and Zn concentrations in Oxygono coast (Lavrio).

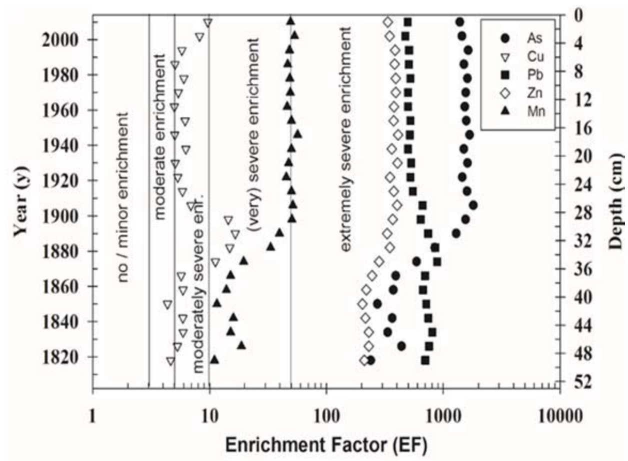

Fig. 5. The enrichment factor profiles of As, Cu, Pb, Zn and Mn.

The minimum and maximum concentrations of As, Cu, Pb and Mn obtained at Oxygono Coast were compared with elemental values at two neighboring areas (Perdica Bay, Delenia Bay) [3], continental crust of earth (shale) [14] and Sediment Quality Guidelines (SEL)[15] (see Table 1). The values obtained at Oxygono Coast were at least one order of magnitude higher for most elemental concentrations compared with those in other areas, revealing the anthropogenic influence in the study area due to mining. The values of ^{226}Ra obtained in Oxygono Coast were lower than the world median value for soil [16].

	As	Cu	Pb	Zn	Mn	Al	^{226}Ra
	(μg g^{-1})						(Bq kg^{-1})
min	500	30	2300	3400	1500	1.4 10^{4}	4
max	4800	200	4800	9000	11000	2.3 10^{4}	17
Perdica Bay	53	8	201	97	342	-	<2
Delenia Bay	35	13	122	144	333	-	9
av. shale[a]	13	45	20	95	850	8·10^{4}	-
SEL[b]	33	110	250	820	1100	-	30[c]

a)Average continental crust (shale) concentrations [14]
b) Sediment guidelines (SEL: Severe Effect Level (biota)) [15]
c) World median of soil [16]

Table 1. The concentrations of As, Cu, Pb, Zn, Mn, Al and ^{226}Ra at Oxygono Coast, neighboring areas (Perdica Bay, Delenia Bay), continental crust of earth (shale) and Sediment Quality Guidelines (SEL).

Enrichment Factor results

The enrichment factor (EF) profiles of heavy metals (As, Cu, Pb, Zn and Mn) estimated for the core sediments, are depicted at Fig 5. The whole core was characterized by extremely severe enrichment in As, Pb and Zn and moderately severe enrichment in Cu. Very severe and severe enrichment was observed in the core's upper and lower part (34-52 cm) part for Mn, respectively. Therefore, the anthropogenic influence was more intense in the last 100 years (0-32 cm). The EFs were also estimated for the neighboring marine regions of Perdica and Delenia Bay (Table 2) and showed severe enrichment in Pb and moderately severe enrichment in As. The EFs of all the other minor elements (Cu, Zn and Mn) indicated minor or no enrichment. Thus, Oxygono coast was more influenced from the anthropogenic (mining) activities comparing to the other areas.

	As	Cu	Pb	Zn	Mn
Perdica Bay*	7	0.3	16	2	0.6
Delenia Bay	4	0.5	10	2	0.6

*Al concentrations of Delenia Bay

Table 2. The Enrichment Factors (Efs) of As, Cu, Pb, Zn and Mn in Perdica Bay and Delenia Bay

CONCLUSIONS

In the present study, radiometric techniques (^{210}Pb, ^{137}Cs) were used to estimate the mean sedimentation rate at Oxygono Coast and the historical records of the contaminated area were reconstrusted. The ^{226}Ra profile was calculated and the positive association among ^{226}Ra profile with Zn and Al profiles was also verified. The values of ^{226}Ra obtained in Oxygono Coast were lower than the world median for soil. However, the minimum and maximum values of heavy metals (As, Cu, Pb, Zn and Mn) were an order of magnitude higher than the neighboring regions, the shale of the continental crust of earth and the sediment quality guidelines, revealing the anthropogenic influence due to mining in the study area. The intensity of this influence was verified by the enrichment factor estimation, revealing a moderate to extremely severe enrichment in the previous years.

Acknowlegdements

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