Instrumental Neutron Activation Analysis (INAA) of Cisadane Estuarine Sediments

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ABSTRACT

Nuclear analytical technique instrumental neutron activation analysis was employed for the multielemental analysis of sediments collected from Cisadane estuary. This analytical technique provides concentration of 20 elements which consist of heavy metals and rare earth elements simultaneously. Two sediments cores were collected using core sampler for determining the distribution of all elements in the depth profiles of sediments. Sediment cores were subdivided into 2 cm increment, dried and sent to reactor for irradiation using thermal flux of $\cdot 10^{13}$ neutrons.cm^{-2}.s^{-1} for 20 minutes in Research Reactor Siwabessy, National Nuclear Energy Agency (BATAN), Serpong. Irradiated samples were measured using a multichannel analyzer (MCA) gamma spectrometer coupled with high purity germanium detector. Analysis of particle size was done since uptake of heavy metals by sediments is particle-size dependent. The results are presented and discussed.

Keywords: Heavy metals, neutron activation analysis, rare earth elements, sediment.

INTRODUCTION

Economical development of a country's or region's economy inevitably result increased environmental pollution. The assessment of contamination levels in aquatic ecosystems can be done by analyzing water, sediments or living organism. In the case water analysis, however it has been establish for a given sampling station, monitored over a long period of time that values tend to vary by several orders of magnitude, even when the samples were collected over short time intervals. Consequently, it is more beneficial to assess the pollution by analyzing either sediments or biota organisms. Biomonitoring also has its associated problems and so analysis of sediments is often the optimum method.

Bottom sediment serves as a reservoir for heavy metals and therefore deserve special consideration in the design of aquatic pollution research studies. An undisturbed sediment column contains a historical record of geochemical characteristics in the watershed. If a sufficiently large and stable sediment sink can be located and studied, it will allow an investigator to evaluate geochemical changes over time, and possibly, to establish baseline levels against which current conditions can be compared and contrasted.

In addition to heavy metals, rare earth elements (REE) have been used as geochemical indicators in sediments. These elements show small differences in their chemical properties, allowing only limited fractionation during weathering and sedimentation. In sediments, REE contents are normalized to standard shale values, thought to represent the average composition of detrital minerals being delivered by rivers to the oceans which is similar to the average composition of the post-Archean upper continental crust. Land-derived sediments that are carried into the ocean or continental basins would thus have generally a flat shale-normalized pattern. However, in certain situations, limited fractionation during weathering and diagenesis can take place.

The most commonly employed analytical technique in environmental studies is certainly Atomic Absorption Spectroscopy (AAS) which is characterized with simplicity of operation, high sensitivity and reliability for a number of toxicologically important metals such as Cd, Hg, Pb, and last but not least, relatively modest cost. The main drawback of AAS is its being a single-element technique and chemical preparation.

Neutron activation analysis (NAA), on the other hand, is a complementary to other analytical methods and a very powerful technique for the non-destructive multielemental in determining element composition of different types of materials for important task in a wide range of disciplines such as biomonitoring, human and other biological analysis, environmental research and material science. Instead of it has a high accuracy and precision, it has also high sensitivity and versatility. Typically 30-40 trace elemental concentrations including

rare earth elements can be determined simultaneously in the marine and environment sample which is needed only in very small amount (1 to 500 mg) of sample.

The objective of this study is to investigate the use of this nuclear analytical technique in sediment analysis and to assess their applicability, accuracies and the limit of quantitative determination (LQD). Sediment cores from Cisadane estuary region have been analyzed for 20 elements including heavy metals (As, Co, Cr, Cs, Fe, Hf, Hg, Na, Sb, Sc, Th, U, and Zn), and rare earth elements (La, Ce, Nd, Sm, Eu, Yb and Lu), and discuss the vertical distribution along core sediments.

MATERIALS AND METHODES

Study area. Sediment cores were obtained from the Cisadane estuary, Tangerang, Banten province. The Cisadane River is the second largest and most important rivers in the Banten province as a resource for industry, agriculture, water supply and natural habitat. The Cisadane river flows to the northern (Java Sea), receives the tributaries from ten small rivers on the upper catchments which originate from Mount Salak in West Java. Many factories and housings built along the river; therefore some of the wastes are discharged to the river and accumulate in the estuary before transporting to the deep sea.

Sampling. Sediment cores were obtained by pushing an open plastic tube with a 7.6 cm diameter and 50 cm length into the estuary mud. The cores were taken from 2 sites of the Cisadane estuary, i.e. left and right side of the small delta (Fig. 1). No compaction of sediments was noted in the core tube during coring.

In the laboratory, sediment cores were sliced at 2 cm interval for heavy metals and Pb-210 analysis. Samples were dried in the oven for 3 days in the temperature of 60^0C and weighted prior and after dried for water contents. For quantitative and quality assurance, two certified reference materials from International Atomic Energy Agency (IAEA-SL-1 and SL-3) and synthetic standards were used to certify the counting system. The synthetic standards which content of several elements were prepared by pipetting standard solution containing each element to a small piece of Whatman paper filter and evaporated to dryness under an infrared lamp. Grain-size analysis of sediment core samples was measured by 200 mesh-wet sieving to determine the sand and silt+clay contents.
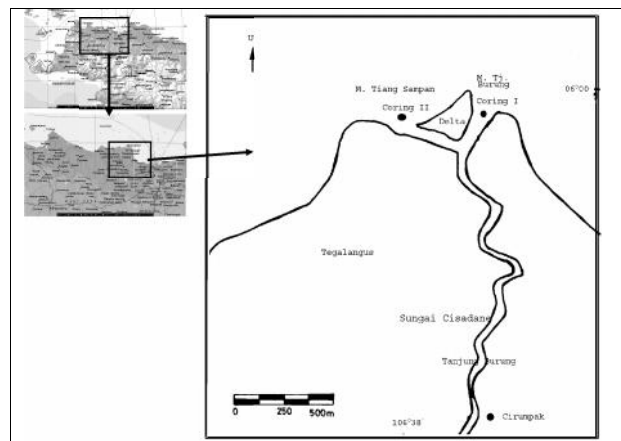

Fig. 1. Map of sampling location of Cisadane estuary

Irradiation. There was no chemical preparation of all samples, dried core sections of sediments were pulverized using agate mortar and pestle. 200 mg of these samples and standards were placed in small polyethylene bags (precleaned with 0.2 M HNO_3), and irradiated with thermal neutrons (thermal neutron flux: ~ 10^{13} n.cm^{-2}.s^{-1}) at the 50 MW Research Reactor Siwabessy, National Nuclear Energy Agency, Serpong, Banten Province for 20 minutes. The counting of activities of the samples could be started at various times ranging from 5 days to 30 days of cooling time after the irradiation performed. The irradiation and counting conditions of elements are tabulated in Table 1. Moreover, the cooling time as well as the counting time depended on the decay time of radionuclides (heavy metals).

Counting. All the measurements were done in the laboratory of marine and sedimentology, Center for the application of isotopes and radiation technology, BATAN. The γ-ray spectrometry analysis was carried out using High Purity Germanium (HPGe) coaxial detector connected to PC-based multichannel analyzer (MCA) with efficiency 10%, resolution (FWHM) 1.89 keV at energy of ^{60}Co 1332 keV, and peak to Compton ratio of 38.1: 1. AccuSpec software was used for data acquisition. The spectrometer was calibrated using multi γ-rays standard ^{152}Eu for qualitative analysis in determining the elements in the samples. The data collected were analyzed quantitatively using SAMPO 90 software relative to standards.

The calculation of heavy metal concentrations uses a relative method which the samples and standards were irradiated simultaneously and measured under identical geometry conditions. This method is simple to use, precise and accurate if the standards is available

Table 1. Irradiation and counting conditions

Irradiation facility	Irradia-tion time	Cooling time	Count time	Nuclides*
TR-1	20 m	5 d	30 m	^{76}As(559.1, 26.3h), ^{197}Hg(77.4, 64.1h), ^{140}La(328.8, 40.23h), ^{24}Na(1368.6, 15.02h), ^{239}Np(U)(277.6, 2.35d), ^{153}Sm(103.2, 46.7h).
		12 d	2 h	^{141}Ce(145.4, 32.5d), ^{51}Cr(320.1, 27.72d), ^{46}Sc(889.3, 83.3d), ^{175}Yb(396.3, 4.19d).
		30 d	5 h	^{60}Co(1073, 5.27a), ^{147}Nd(91.1, 10.99d), ^{134}Cs(795.9, 2.06a), ^{152}Eu(1408, 13.4a), ^{59}Fe(1099.3, 44.5d), ^{181}Hf(482.2, 42.4d), ^{177m}Lu(378.5, 160d), ^{233}Pa(Th)(312.1, 27.0d), ^{124}Sb(1691.0, 60.2d), ^{65}Zn(1115, 243.8d).

* The values in brackets are the energy γ-ray in keV and half life

Tabel 2. Typical Limit of Quantitative Determination (LQD) achievable on 200 mg sample size of standard with 6 days after irradiation at neutron flux of $\sim 10^{13}$ n.cm^{-2}.s^{-1}

Elements	LQD (ppm)	Elements	LQD (ppm)
As	0.12	Eu	0.37
Ce	3.38	La	0.24
Co	1.53	Lu	0.02
Cr	4.91	Nd	5.31
Cs	1.92	Sm	0.04
Fe	0.72	Yb	0.27
Hf	0.69	Sb	0.25
Hg	0.01	Th	0.42
Na	0.98	U	1.51
Sc	0.72	Zn	0.55

Table 3. Comparison of some elements between present work and certified values for the standard (IAEA-SL-1)

Element	Certified (ppm)	Range (ppm)	Present work (ppm)	Range (ppm)
As	27.6	24.7–30.5	28.1	24.2–32.0
Co	19.8	18.3–21.3	18.5	16.0–21.0
Cr	104	95–113	103	90–116
Fe	67400	65700–69100	64600	62600–66600
Sc	17.3	16.2-18.4	17.1	15.6-18.6
Zn	223	213–233	225	210-240

similar in composition to the sample. It eliminates many errors such as those to flux parameters, nuclear data, decay scheme, efficiency, self shielding, coincidence summing, etc. The formula is:

$$W_s = \frac{A_s \exp^{\}T_s}}{A_{st} \exp^{\}T_s}} . W_{st}$$

where

W_s = weight of element being sought in the sample;

W_{st} = weight of the element in the standard;

A_s = count rate of sample; A_{st} = count rate of standard;

$\}$ = decay constant ($\ln 2 / t_{1/2}$) of the radioisotope;

LQD is given in Table 2 were determined by INAA on sediment by irradiation of 200 mg of IAEA SL-1 at a flux $\sim 10^{13}$ n.cm^{-2}.s^{-1} for 20 minutes with a counting time of 30 minutes after a decay of 6 days. The electronic dead-time in all measurements was less than 10%.

RESULTS AND DISCUSSION

To confirm the accuracies and sensitivities of analytical methods used in this study for quality assurance, some elements of standard reference material (IAEA- SL-1) were analyzed and presented in

Table 3. Results are generally in a good agreement with certified values. In order to maintain the capabilities in analyzing samples, laboratory has been participating in inter-comparison exercise and proficiency test organized by local and international in different types of environmental samples.

A total of about 40 γ-ray lines were observed. The elements producing γ-ray lines were As, Co, Cr, Cs, Fe, Hg, Na, Sc, Th, U, Zn, Ce, Eu, Hf, La, Lu, Nd, Sb, Sm and Yb. Fig. 2a and Fig. 2b show a portion of the γ-ray spectrum in the region between 0 to 300 keV and 300 to 1500 keV for the sample sediment after 12 days irradiation from Cisadane estuary, respectively. Meanwhile, the background of the γ-ray spectrum which was measured in the period of measurement is shown in Fig. 3a and Fig. 3b. In comparing to the count/ channels of γ-ray spectrum of samples, the count/ channels of background are very small for each of elements. In addition, the SAMPO software reduces the background automatically in calculating the concentration of interested elements.

The silt+clay contents of sediment cores from Cisadane estuary are given in Fig. 4. The silt+clay content in core I varied from 65% to 92% with the average of 78% and in core II varied from 55% to 86%
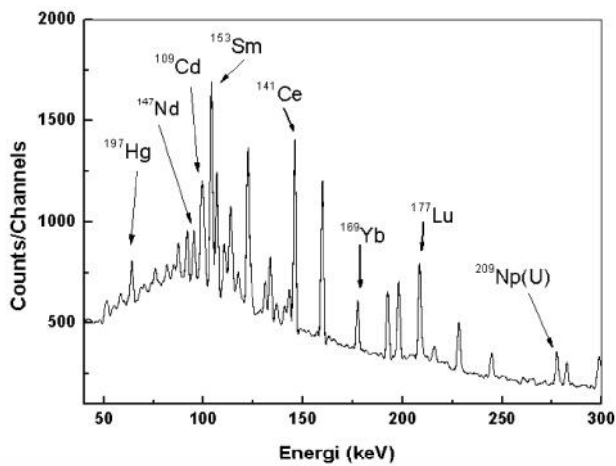
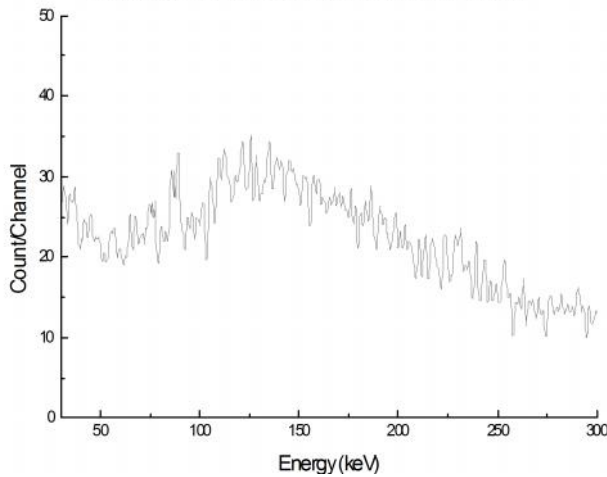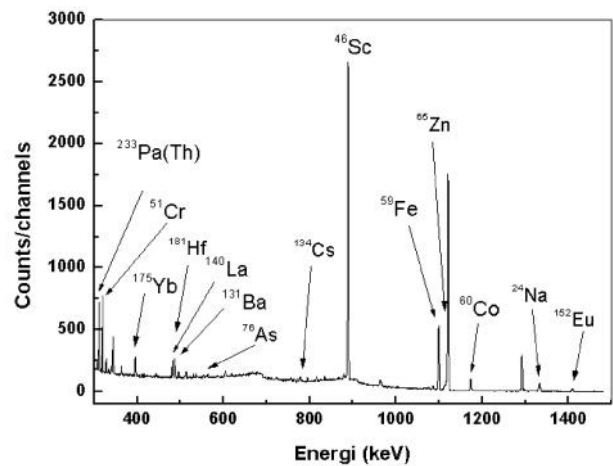Fig. 2a. γ-ray spectrum of sample sediment after 12 days irradiation. The energy from 0 keV to 300 keV

Fig. 2b. γ-ray spectrum of sample sediment after 12 days irradiation. The energy from 300 keV to 1500 keV

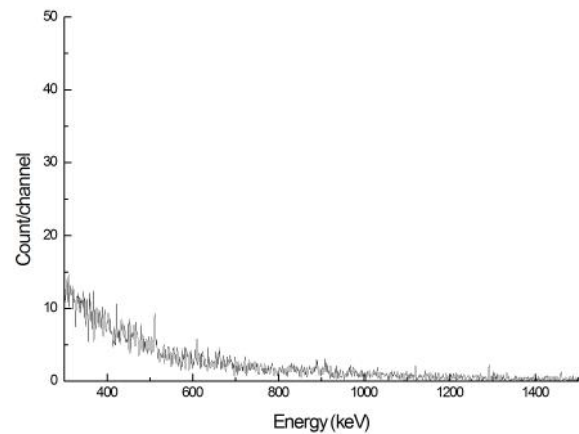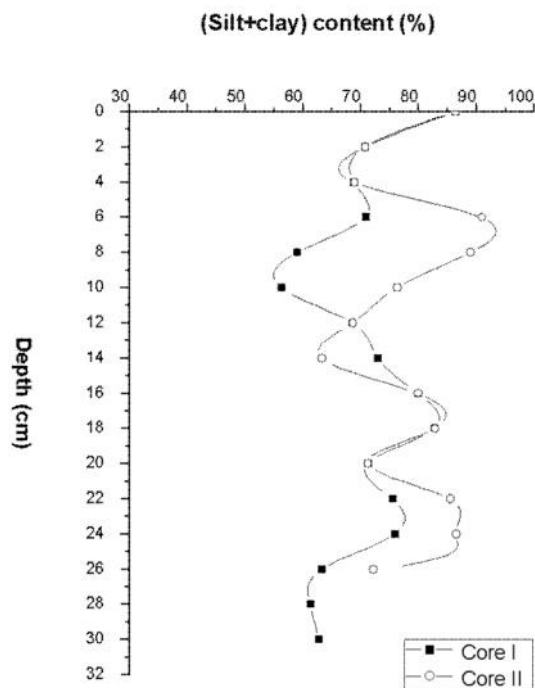Fig. 3a. γ-ray spectrum of background of measurement. The energy from 0 keV to 300 keV

Fig. 3b. γ-ray spectrum of background of measurement. The energy from 300 keV to 1500 keV

Fig. 4. Distribution of silt+clay content in sediment core I & core II

with the average of 70% which indicated the sediment in both cores from Cisadane estuary dominated by silt+clay as prevalence of settling processes. The profiles of silt+clay in both cores are quite similar except on the depth between 4 cm and 12 cm. Moreover, on these depths were identified as the minimum of silt+clay content of core I (10 cm) and the maximum of silt+clay content of core II (6 cm).

Heavy metals. The concentrations of 20 elements were determined in 2 sediment cores. They are grouped as heavy metals (As, Co, Cr, Cs, Fe, Hf, Hg, Na, Sb, Sc, Th, U, and Zn), and rare earth elements (La, Ce, Nd, Sm, Eu, Yb and Lu), result of analysis heavy metals are depicted in Fig. 4a and Fig. 4b for core I and Fig. 6a and Fig. 6b for core II. The average concentrations in ppm of As, Co, Cr, Cs, Fe, Hf, Hg, Na, Sb, Sc, Th, U, and Zn in core I are 7.60±3.71, 15.07±3.43, 9.48±3.30, 0.69±0.13, 56682.5±6573.6, 2.51±0.84, 0.13±0.09, 18453.5±4864.7, 0.30±0.16, 19.71±2.68,
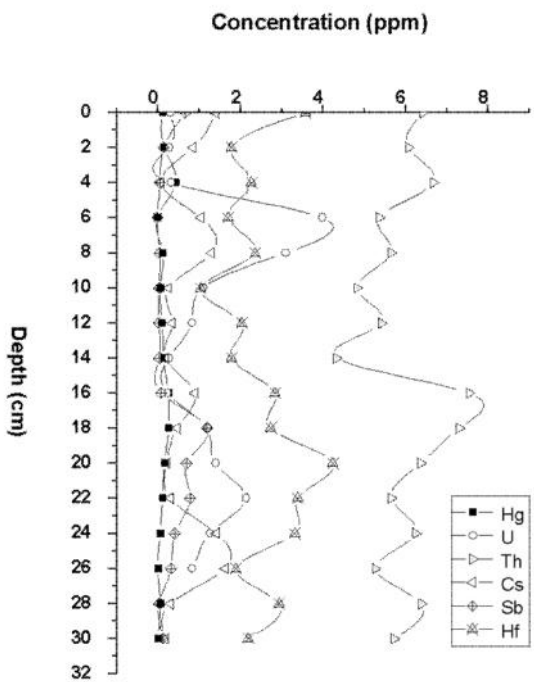
Concentration (ppm)

Fig. 5a. Vertical distributions of heavy metals (Hg, U, Th, Cs, Sb and Hf) in sediment core I
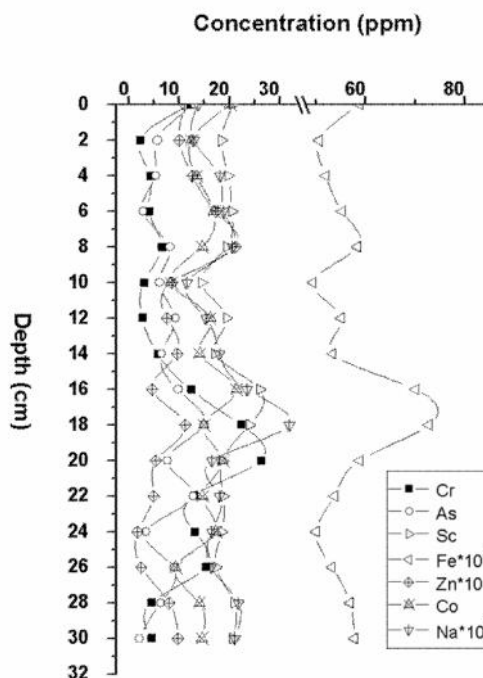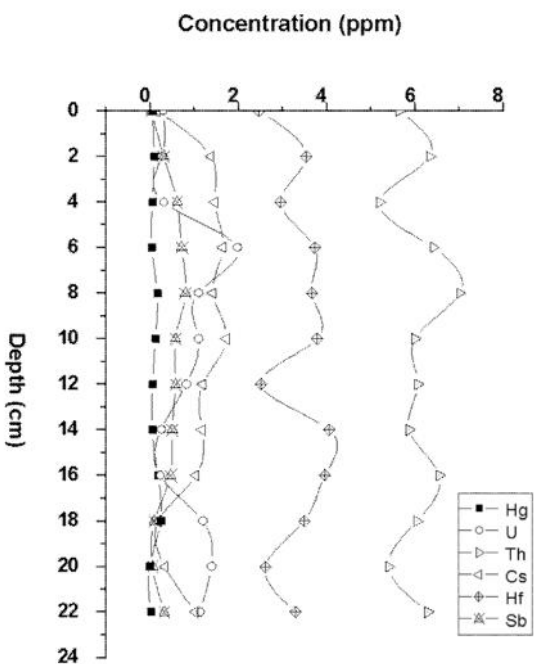
Concentration (ppm)

Fig. 5b. Vertical distributions of heavy metals (Cr, As, Sc, Fe, Zn, Co and Na) in sediment core I

Concentration (ppm)

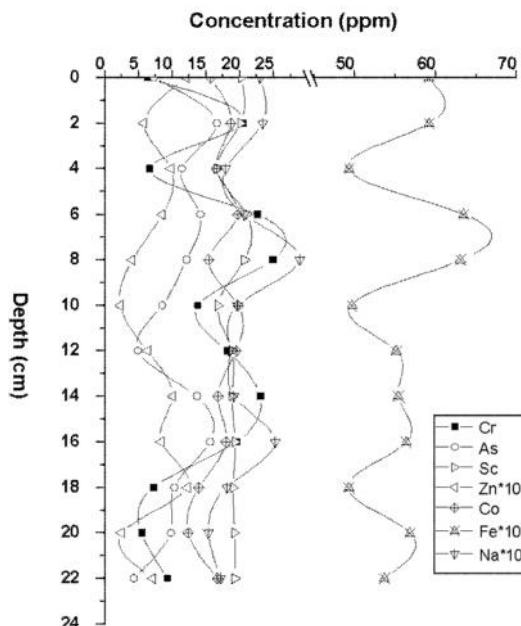Fig. 6a. Vertical distributions of heavy metals (Hg, U, Th, Cs, Sb and Hf) in sediment core II

Concentration (ppm)

Fig. 6b. Vertical distributions of heavy metals (Cr, As, Sc, Fe, Zn, Co and Na) in sediment core II

5.97±0.85, 1.23±1.03, and 91.6±21.1, respectively. While the average concentrations in ppm of these elements in core II are 10.73±3.99, 16.97±2.34, 14.81±2.46, 1.07±0.25, 55926.7±4899.2, 3.34±0.56, 0.09±0.07, 20626.7±3866.2, 0.43±0.15, 19.23±1.36, 6.07±0.50, 0.84±0.17, and 74.8±13.8, and respectively.

The concentration of all elements in core I (Fig. 5a and 5b) were slightly constant from the surface to the

depth of 12 cm and increased to a depth of 18 cm and thereafter not varying to the bottom except for Hg, Cs, Co and U. Hg and Co were found slightly constant along the core, whilst Cs and U both had similar profiles which increased significantly from top to the depth of 6 cm and slightly constant from 10 cm to the bottom. The vertical distribution of mostly all elements seems to be dependent on grain-size profile along a core. Low
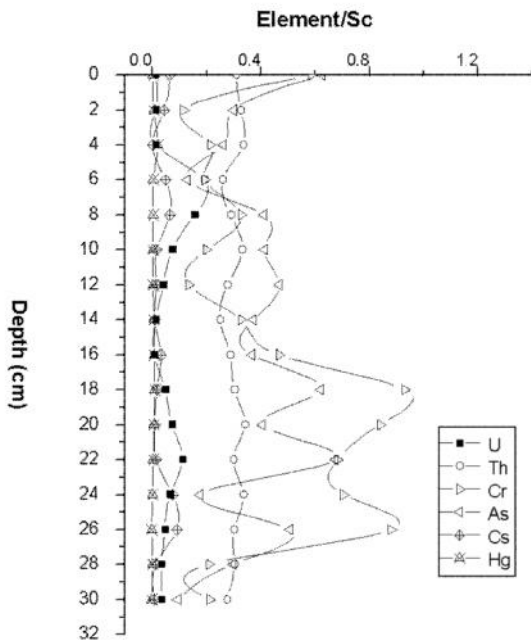
Fig. 7a. Heavy metals (Hg, U, Th, Cs, Sb and Hf) distribution in sediment core I. Concentrations normalized to Sc
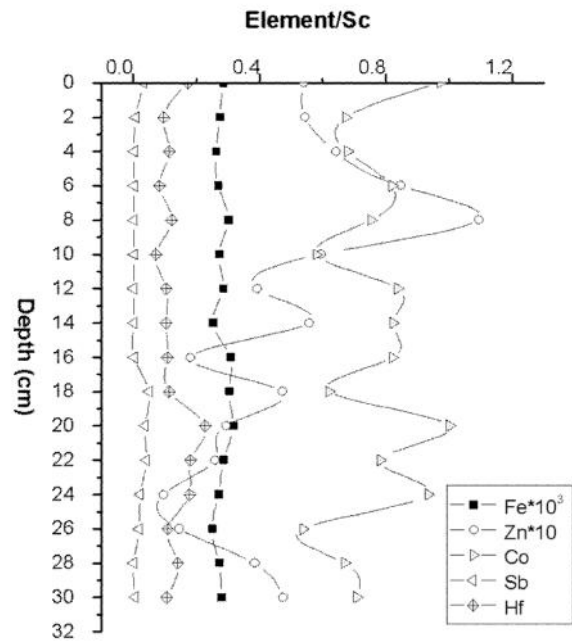

Fig. 7b. Heavy metals (Cr, As, Sc, Fe, Zn, Co and Na) distribution in sediment core I. Concentrations normalized to Sc
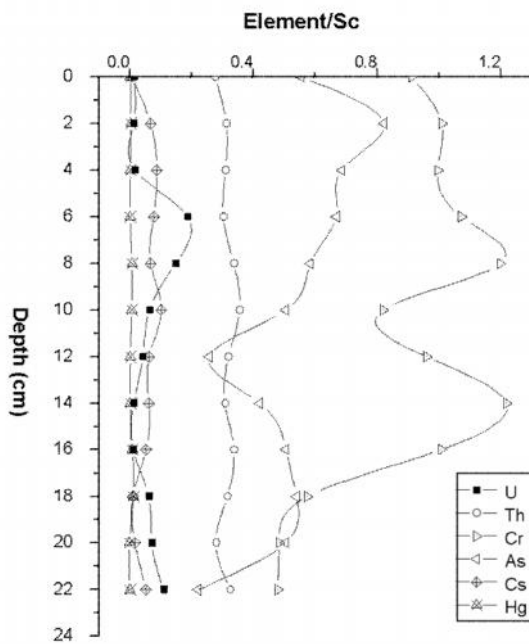

Fig. 8a. Heavy metals (Hg, U, Th, Cs, Sb and Hf) distribution in sediment core II. Concentrations normalized to Sc
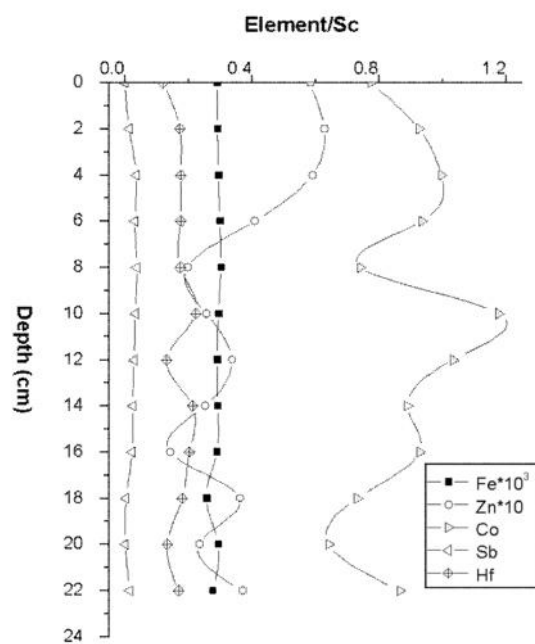

Fig. 8b. Heavy metals (Cr, As, Sc, Fe, Zn, Co and Na) distribution in sediment core II. Concentrations normalized to Sc

concentrations for these elements were observed in the layer where the sands with a coarse sandy fraction dominant, while high concentrations were the fine fraction are dominant (see Fig. 2, Fig. 5a and Fig. 5b). This is in agreement with Randle et al. (2001) as the elemental absorption more preferable to the fine particle than coarse particle. Similarly, the depth distributions of concentration of all elements from core II have a

fluctuation similar to the silt+clay profile, it seems to be dependent on the grain-size distribution except Hg, Cs, Co and U (Fig. 2, Fig. 6a and Fig. 6b).

Another method using normalizing the concentration of the determined elements to a conservative element(s), instead of effect of grain-size can be used in evaluating the vertical distribution of heavy metals along the core. Potential elements for
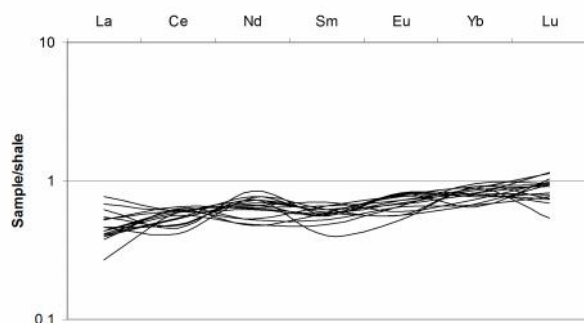
Fig. 9a. Shale-normalized REEs pattern for sediment core I

Fig. 9b. Shale-normalized REEs pattern for sediment core II

this purpose are Al, Cs, Fe, Sc and Rb which, in addition to their grain size dependence are not influenced anthropogenically. In the analyses that follow, however, we use Sc for normalizing the vertical element concentrations, since Sc is highly favorable nuclear characteristic for INAA.

The ratio of a given element concentration to that of Sc, the vertical distribution of Cs, Hg, Th, U, Fe, Sb and Hf in bulk samples from of core I (Fig. 7a and 7b) and core II (Fig. 8a and 8b) show little or no variation with depth, indicating that an anthropogenic input for these elements in unlikely or that if there was one it was very constant with time. On the other hand, vertical distribution of Cr, As, and Co in core I slightly constant in the uppermost of 16 cm, and significantly change from the depth 16 to the bottom. However, Zn has a particular fluctuation in the profile of core I, which has high concentration on the depth of 6 cm and thereafter decreased significantly to the depth of 26 cm and increased to the bottom. The fluctuation of the elements which were normalized to Sc indicated contamination.

The enrichment factor (EF) which was used to show the influence of industrial pollution, concentrations of top 4 and bottom 4 layers (corresponding to 8 cm each) was calculated for Cr, As, Co and Zn element. The result shows that EFs for Cr, As, Co and Zn in core I are 0.72, 0.99, 0.97, and 2.51, respectively. Meanwhile, the EFs for Cr, As, Co and Zn in core II are 0.82, 1.09, 1.10, and 2.01, respectively.

Rare earth elements. The average concentrations in ppm of La, Ce, Nd, Sm, Eu, Yb, and Lu in Core I are 21.59±3.55, 3.33±0.41, 40.89±5.14, 2.51±0.29, 0.43±0.09, 15.45±4.02, 0.86±0.12, respectively. And the average concentrations in ppm of La, Ce, Nd, Sm, Eu, Yb, and Lu in Core II are 17.96±3.63, 4.05±0.71, 42.64±5.03, 1.88±0.14, 0.42±0.05, 16.44±3.42, 0.78±0.13, respectively.
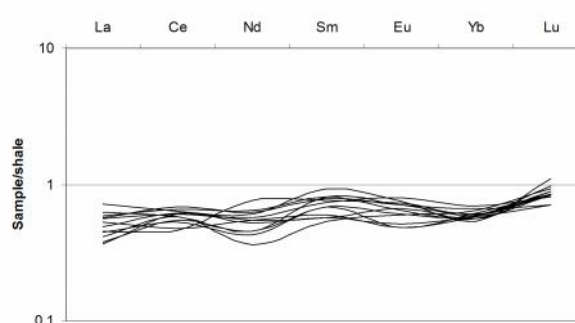
The normalization procedure used the REE average concentrations in the NASC (North American Shale Composite): La = 32 ppm, Ce = 73 ppm, Nd = 33 ppm, Sm = 5.7 ppm, Eu = 1.24 ppm, Yb = 3.1 ppm, and Lu = 0.48 ppm. Fig. 8a and 8b display the shale-normalized REEs pattern for sediments in both cores. Moreover, the REEs were arranged from the light REE to the heavy REE. The REE patterns of the analyzed samples in core I and core II are uniformly flat and similar as shown in Fig. 9a and Fig. 9b. A comparison on the distribution of REEs in both core sediments investigated in this study to those obtained from average shale could be explained that almost all of REE concentrations lower than the shale value (< 1).

CONCLUSION

The effective applicability of the INAA for environmental marine samples has been proven by the results of numerous studies. This method requires no chemical sample preparation, and is accuracy and sensitivity. In this study as an application of INAA, twenty elements in sediment core samples from Cisadane estuary were determined simultaneously with an analytical quality control. The profiles of heavy metals concentration in both cores show no significant differences since the locations receive similar amount of elements from the Cisadane River. Moreover, these profiles are sedimentary facies dependent which are preference for the fine fraction. REE distribution patterns in sediments collected from study site did not show significant variations, suggesting an efficient mixing of the provenance components and a constant REE fractionation in the sediments. The flat and similar REE distribution patterns have the value lower than the average shale.

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