J.Sci.Soc.Thailand, 22 (1996) 313-324

PB-210 RADIOMETRIC DATING OF ESTUARINE SEDIMENTS FROM THE EASTERN COAST OF THAILAND

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(Received July 1, 1996)

ABSTRACT

Eighteen sediment cores were taken from the Bang Pakong and Chantaburi River estuaries. The excess Pb-210 concentration profiles obtained were used to calculate annual sedimentation rates and thus the age profiles of the cores. The dating model assumes a constant flux of Pb-210 from the decay of atmospheric Rn-222, followed by adsorption on suspended particulates which carry the Pb-210 to the estuarine sediments at a constant rate. The results of investigation showed higher values of sedimentation rate of Bang Pakong River mouth than those from Chantaburi River mouth. This is probably due to dramatic decrease of the mangrove forests in the area and as a result of diagenetic remobilization of Pb-210 in the deeper sections of the sedimentary column.

INTRODUCTION

The estuarine sediments are a complex mixture of materials introduced through rivers, shoreline erosion, *in situ* biological and chemical processes and from human sources. These sediments thus store in them information about these sources, in particular the temporal variations in their rates of supply. There is a strong need to obtain data on these variations, especially those due to man. Documentation of such changes requires a chronological study of the sediment core, as well as knowledge of the distribution of relevant chemical species in sediments.

In the past few decades many applications of natural and man-made radionuclides to the determination of sediment accumulation rates have been documented[1,2,3,4]. These methods have provided useful information in some cases, but in many others they have met with only limited success, since post-depositional processes (such as biological and physical mixing, erosion) confounded the record. These processes tend to alter the sequence of events stored in the sediment column or even erase them, making the geochronological studies difficult. In spite of this, in the last few years it has been possible to understand the effects these various processes have on radionuclide distribution in the sediment column, and to establish the chronology of sediment accumulation and other sedimentary processes in estuaries. This study investigated the sediment-accumulation rates in the estuarine sediments from the eastern coast of Thailand. Such information may enable a reasonable estimate of the background level and changes in input of some pollutants over an extended period of time[5,6].

MATERIALS AND METHODS

Pb-210 is a naturally occurring radioisotope of the U-238 family (Fig. 1). Its closest parent with a significant half-life is radon 222 (Rn-222, half-life: 3.8 days; Fig.1)

U-238 →→→ Ra-226 → Rn-222 → Po-218 → Pb-214 → Bi-214
(1622 y) (26.6 m) ↓ ↓

Pb-206 ← Po-210 ← Bi-210 ← Pb-210 ← Po-214
(stable) (22.3 y)

Fig. 1. Decay scheme of Ra-226 and its daughters. These isotopes belong to the U-238 series[1].

which being a noble gas, escapes into the atmosphere from surface soil layers and provides lead-210 with an unexpected mobility. This mobility creates an "excess" of lead-210 (Fig.2) compared to those expected from secular equilibrium with radium-226 (Ra-226, half-life: 1622 years; Fig.1) which forms the basis of the lead-210 dating method. Lead-210 is introduced into the estuarine environment through atmospheric precipitation, terrestrial run-off and *in situ* production from radium-226 in the water column. Studies of the behavior of lead-210 in continental waters[7] and its budget in shallow coastal areas show that atmospheric precipitation is its dominant pathway to estuaries. Lead-210 once introduced in the estuarine and near coastal water is removed quickly to sediments by adsorption/scavenging processes[5] (Fig.2).

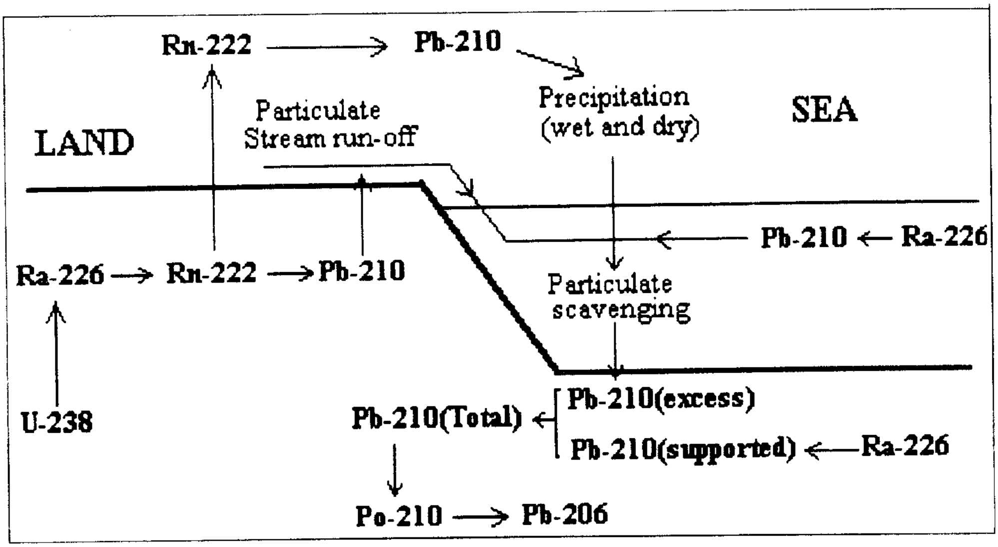

Fig. 2. Potential sources of Pb-210 in marine sediments (modified from Bruland *et al.*[5]).

The mean residence time of lead-210 in the Long Island Sound waters was reported by Beninger *et al.* to be only a few months8. The fast removal of lead-210 from coastal waters has incited efforts to use it as a dating tool in these areas. Initial tests for the lead-210 dating method were made on sediments of the Santa Barbara Basin[2]. In addition this method was proven successful in the dating of marine deposits of the continental margins[5] and estuarine regions[9].

This dating method is based on the assumptions of constant flux of lead-210 to the sediments over the sampling interval and insignificant mobility of lead-210 in the sediment column. If these conditions are met and if the sediment-accumulation rate has remained constant over the sampling interval, then the lead-210 excess activity Az, at depth, z, from the sediment-water interface is given by

$$A_z = A_o \exp(-\lambda z/s) \quad (1)$$

where Ao is the lead-210 excess activity at the interface, λ is the radioactive decay constant (y^{-1}) of lead-210 and s is the sediment accumulation-rate in centimetres per year. A plot of ln A versus depth yields a straight line with the slope $(-\lambda/s)$.

Core sampling

Core samples 7 cm in diameter, were taken mostly from the Bang Pakong River estuary, Chonburi province. The sampling location for sediment core samples is shown in Fig. 3. Station 1, 2, 3, 4 and 5 represent the estuarine, industrial, agriculture, urban, and reference areas respectively. In addition, a core sample was also taken from Chantaburi River Mouth, Chantaburi province for comparison. The coordinates of sampling stations are given in Table 1. Core samples were obtained using pre-cleaned PVC tubes. The tubes were immediately sealed at both ends with plastic sheets. One-centimeter sections at every 3-cm intervals were obtained from the cores using a plastic knife. This was done up to a depth of 10 cm, afterwhich 1-cm sections were taken at 5-cm intervals below that depth. The sediment subsamples were freeze-dried, ground and homogenized in an agate mortar, and sieved through a nylon sieve (2 mm mesh size) to eliminate the coarse fragments.

TABLE 1. Sampling location.

sampling area	station	N	E
Bang Pakong River	1	13° 27' 34"	109° 58' 02"
	2	13° 32' 49"	101° 00' 17"
	3	13° 35' 49"	101° 04' 56"
	4	13° 40' 53"	101° 04' 44"
	5	13° 51' 05"	101° 09' 23"
Chantaburi River mouth	6	12° 50' 10"	102° 08' 15"

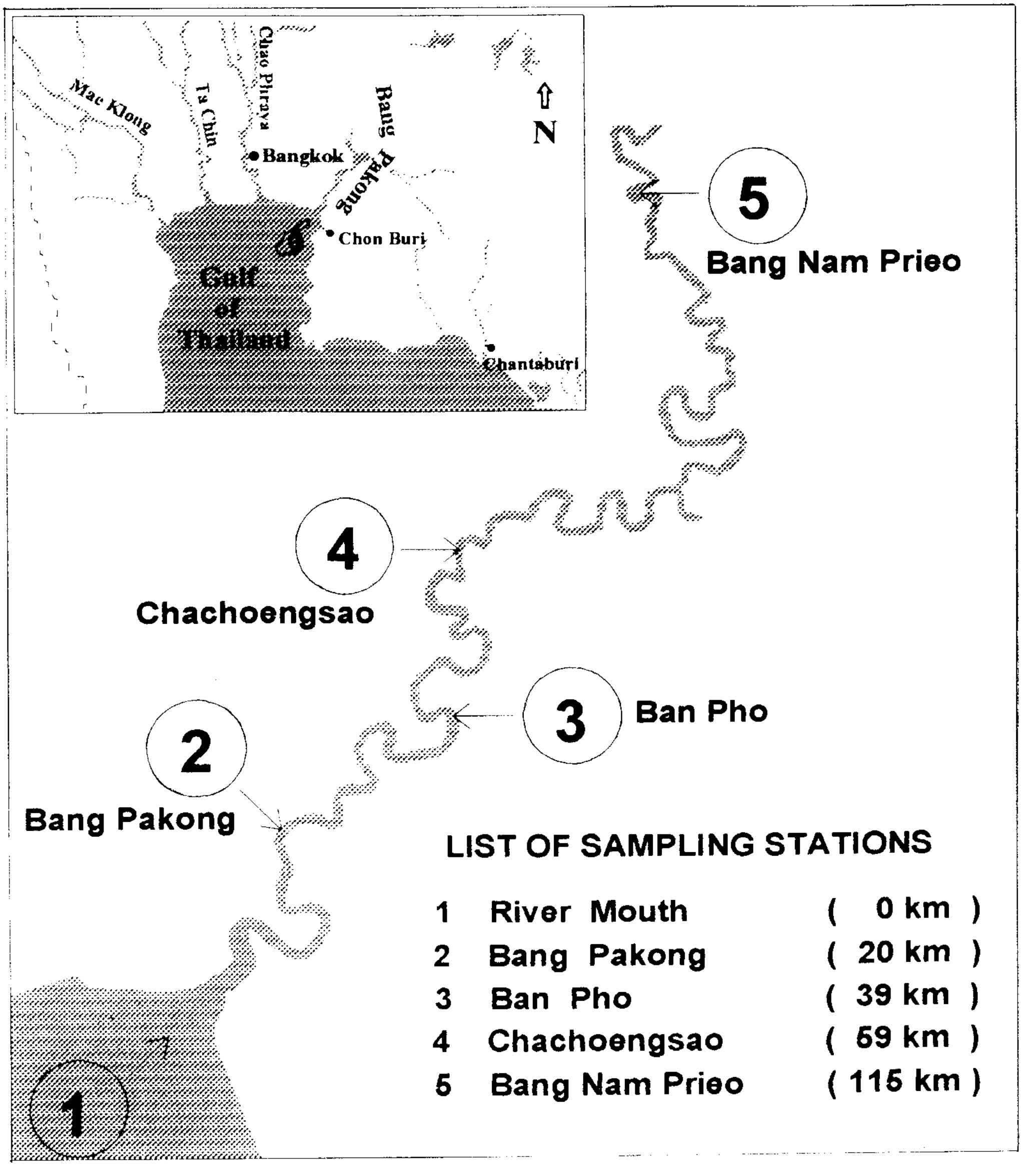

Fig. 3. Sampling Station along the Bang Pakong River.

Dating techniques

The chemical procedures described by Farmer[3], Nittrouer *et al.*[10], and Carpenter *et al.*[11] were used in the Pb-210 radiometric dating of sediments. Pb-210 activity was determined by alpha spectrometry of its granddaughter Po-210 by assuming that Pb-210 and Po-210 are at secular equilibrium. An example of the alpha spectrum of Po-210 and standard Po-209 is shown in Fig 4. Under the assumption of constant Pb-210 deposition rate and with no postdeposition migration, the net Pb-210 activity from atmospheric deposition in the sediment cores should decrease with depth after correction for the supported lead from local Ra-226. If these conditions are met, then the excess Pb-210 activity (Az) at depth z from the sediment-water interface is given by equation (1).

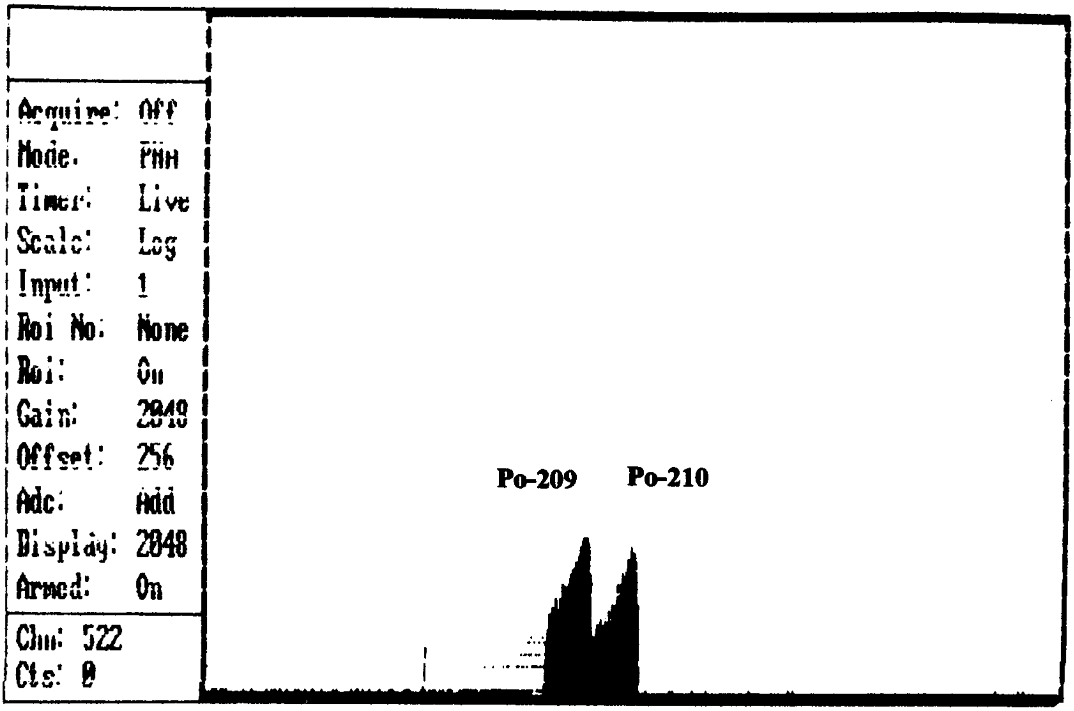

Fig. 4. Relative positions and alpha spectrum of Po-210 and standard Po-209 peaks measured by alpha spectrometer (Ortec ion-implanted silicon partially depleted charged-particle detector coupled to Tennelec multichannel analyzer).

Estimation of porosity and sediment-accumulation rate

The wet sediment sections were freeze-dried and the water content determined from the weight loss. Porosity (() values were obtained using the relationship

$$\phi \quad = \quad \frac{Mw/\rho w}{Mw/\rho w + Ms/\rho s} \qquad (2)$$

where Mw and Ms are the masses and ρw and ρs are the densities of water and solids in the sediment, respectively.

The sediment-accumulation rate (F in $g/cm^2/yr$) may be calculated as follows[12]

$$F \quad = \quad S\,(1 - \phi)\,\rho \qquad (3)$$

where R is the sedimentation rate (cm/yr), ϕ is the porosity, ρ is the dry density of the sediment (g/cm^3).

RESULTS AND DISCUSSION

The sedimentation rates were determined by Pb-210 method.[3,10,11] The Pb-210 supported by Ra-226 was substracted from the total Pb-210 activity to give an excess Pb-210 values by utilizing the average Pb-210 activities (0.45 dpm/g) in the deeper sections of the core where the total Pb-210 activity appears to be constant. The excess Pb-210 depth profiles of the sampling stations are shown in Fig.5. All profiles showed exponential decreases in the excess Pb-210 activity from the surface to the deeper strata with no indication of a surface "mixing zone". This may be due to loss of surficial sediments when lowering the cover into clay-rich sediments. As the corer penetrated the sediment, the upper mixed zone was probably pushed aside, with the corer retaining only the more consolidated sediments below.

The sedimentation rates for station 1-5 of the Bang Pakong River Estuary sediment were found to be 0.69, 0.74, 0.57, 0.48, and 0.46 cm/yr respectively whereas the sedimentation rate at the Chantaburi River mouth (station 6) was found to be 0.56 cm/yr. Similar sedimentation rate of about 0.54 cm/yr for the Bang Pakong River mouth was reported by Windom *et al.*[13]

The results of the investigation (Table 2) showed higher value of sedimentation rate of Bang Pakong River mouth (station 1, 0.69 cm/yr) than Chantaburi River mouth (station 6, 0.56 cm/yr) (Fig. 6). This is probably due to dramatic decrease of the mangrove forests in the Bang Pakong Basin, since mangroves play an important role in stabilizing shorelines in coastal streams and estuaries by protecting them against tidal bores, and soil erosion. The main conversions of mangrove forests in the area have been to aquaculture,salt pond construction, urbanization, industrialization and harbor construction.

Table 2. Mean of excess Pb-210 activity (dpm/g), density (ρ in g/cm^3), porosity (ϕ), sedimentation rate (R in cm/yr), and sediment-accumulation rate (F in g/cm^2/yr) of the sampling areas.

Sampling area	Station	Depth (cm)	Mean of excess Pb-210(dpm/g)	S.D.	ρ (g/cm^3)	ϕ	S (cm/yr)	F (g/cm^2/yr)
Bang Pakong River	1	1	4.2	0.20	2.00	0.82	0.69	0.25
		10	3.6	0.15	1.98	0.76		0.33
		20	1.8	0.16	2.03	0.69		0.43
		30	1.1	0.15	2.00	0.68		0.44
	2	1	8.6	0.10	2.11	0.79	0.74	0.33
		10	5.3	0.15	2.12	0.69		0.49
		20	3.8	0.21	2.11	0.67		0.52
		30	2.0	0.20	2.05	0.62		0.58
	3	1	7.4	0.20	2.10	0.78	0.57	0.25
		10	5.4	0.15	2.13	0.75		0.30
		20	2.3	0.10	2.13	0.72		0.34
		30	1.6	0.15	2.12	0.69		0.37
	4	1	6.0	0.20	2.12	0.79	0.48	0.21
		10	2.9	0.21	2.06	0.76		0.24
		20	1.2	0.21	2.13	0.71		0.30
		30	0.9	0.20	2.12	0.68		0.33
	5	1	6.0	0.21	2.25	0.79	0.46	0.22
		10	3.1	0.15	2.20	0.76		0.24
		20	2.1	0.20	2.18	0.71		0.29
		30	0.7	0.15	2.15	0.65		0.35
Chantaburi River mouth	6	1	4.1	0.15	2.12	0.86	0.56	0.18
		10	3.3	0.21	2.11	0.85		0.17
		20	1.2	0.10	2.11	0.82		0.21
		30	0.9	0.15	2.11	0.80		0.24

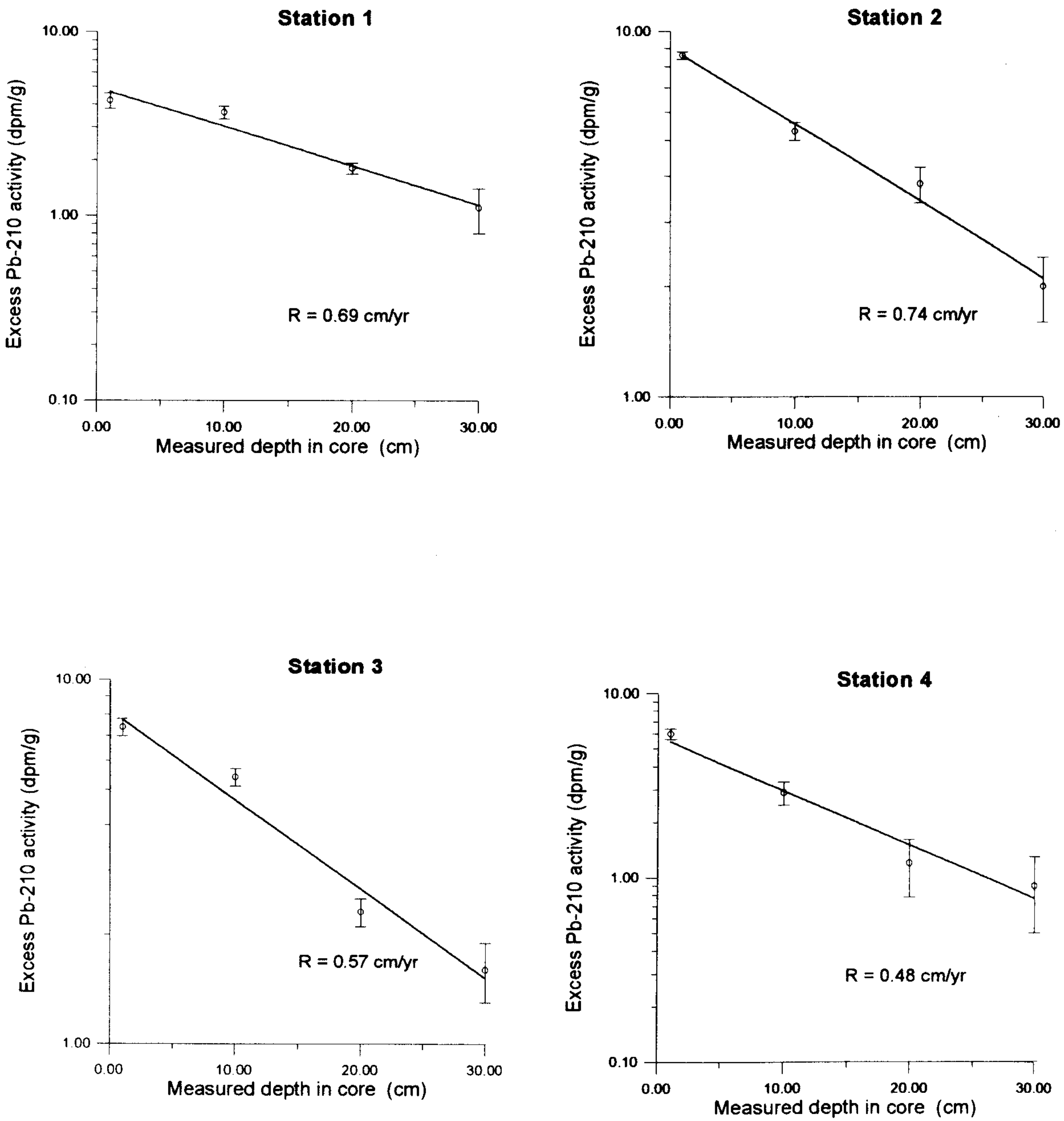

Fig. 5a. Excess Pb-210 as a function of depth in sedimentary column from Bang Pakong (Station 1-4).

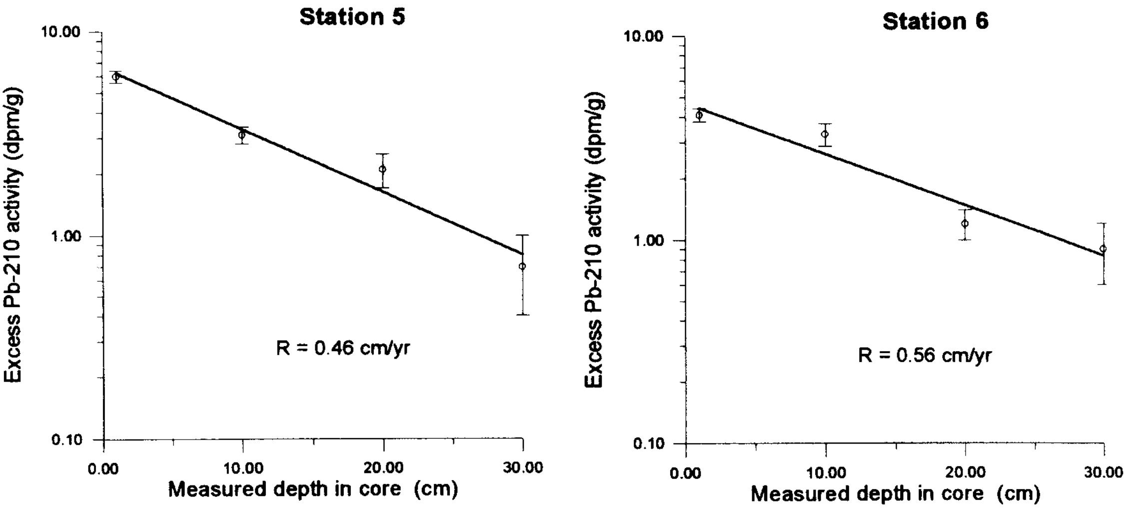

Fig.5b. Excess Pb-210 activities as a function of depth in sedimentary column from the Bang Pakong and Chantaburi River estuary (Station 5,6).

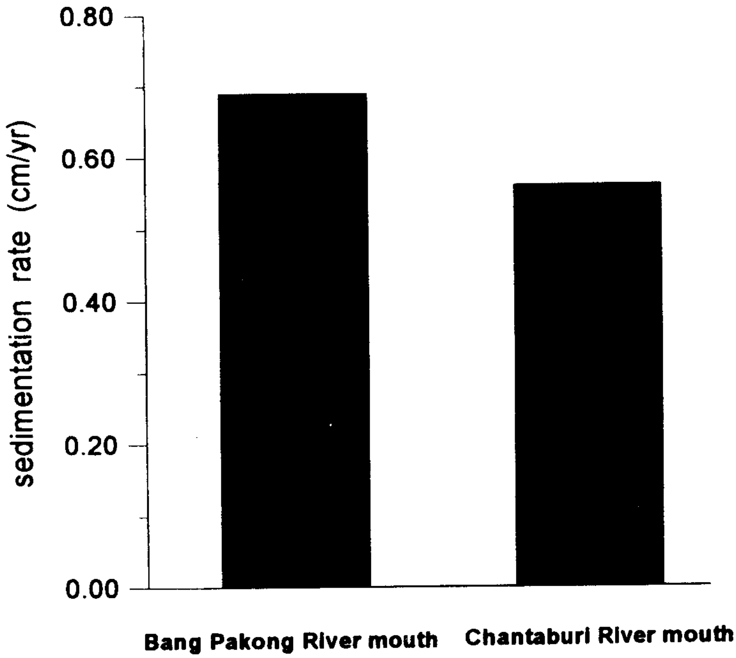

Fig. 6. Comparison of the sedimentation rates of Bang Pakong and Chantaburi River mouth.

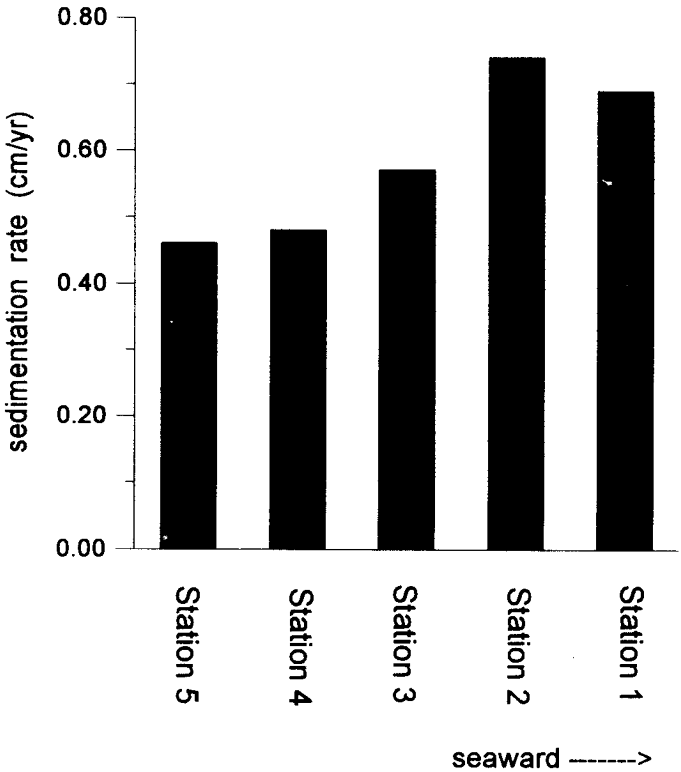

Fig. 7. Sedimentation rates of the Bang Pakong River estuary.

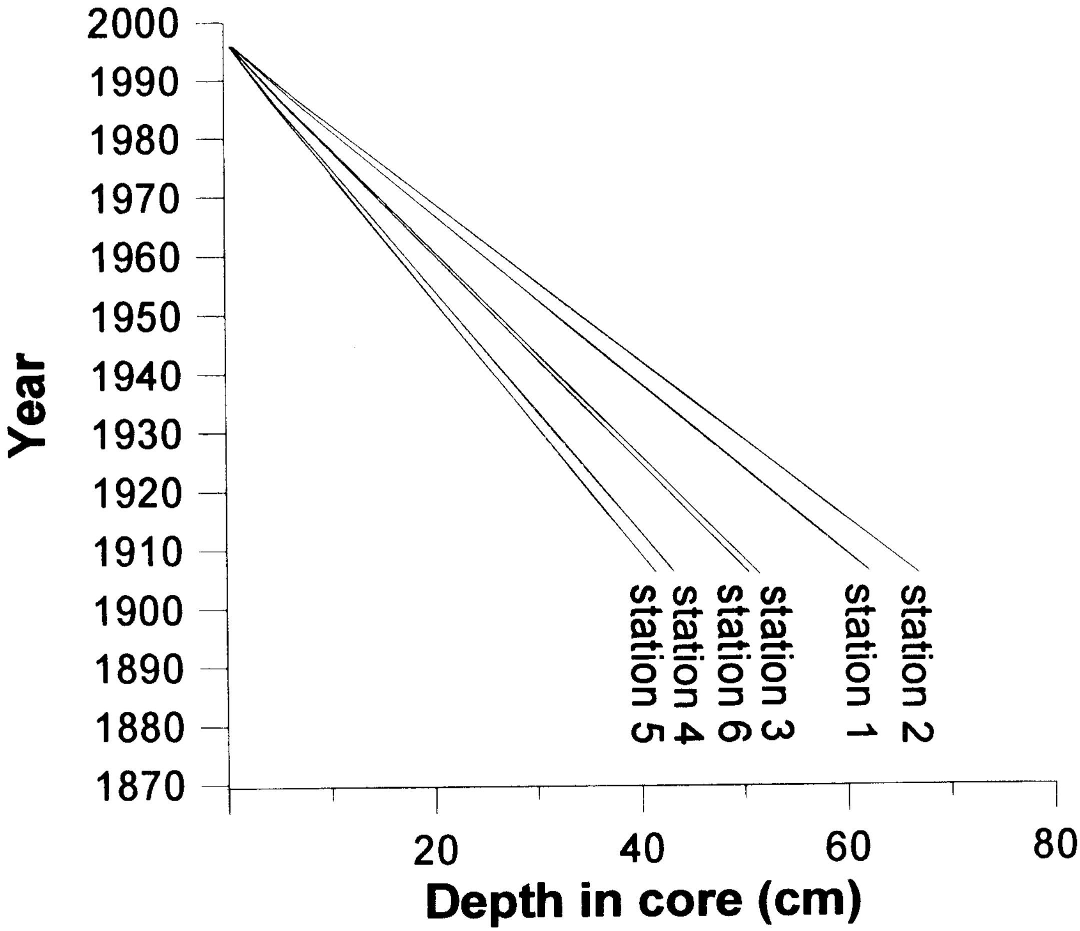

Fig. 8. Pb-210 age versus depth in core

Data obtained by Cheevaporn *et al.*[14] showed that the redox potential (Eh) in the deeper sections of the sedimentary cores from the Bang Pakong River Estuary become more reducing as evidenced by decreased Eh and increased hydrogen sulfide concentrations in the sedimentary column. It is possible that some Pb-210 may have been remobilized from depths in relation to iron and manganese diagenesis (under the reducing environment) as described by Benoit and Hemond.[15] Loss of Pb-210 from the deeper sections of the Bang Pakong sedimentary column in relation to the upper sections, results in the greater value of the slope ($-\lambda/s$) yields from the plot of ln **A** versus depth (see equation 1). Eventually, a higher sedimentation rate than actual value may be obtained from the study as a result of early diagenetic processes involving Pb-210 in the sedimentary column.

The results of the investigation also showed that the sedimentation rates in the Bang Pakong River increase towards the river mouth (Fig. 7). This character is usually attributed to the decrease in velocity of the stream near the river mouth and/or the mixing of marine sediment in the transition zone near the river mouth. However, the available data are not sufficient to provide an adequate description. Further investigation is still needed.

The results of sediment-accumulation rate (F in Table 2.) which is obtained from equation (3) indicate that sedimentary fluxes of the Bang Pakong River were mostly higher than those in the Chantaburi River. This implies that the Bang Pakong River has higher mass input rates than the Chantaburi River. Results of the statistical analysis at 95 and 99% confidence level (t-test) revealed that significance does exist between means of the sediment-accumulation rate of Bang Pakong River estuary(mean = 0.36 $g/cm^2/yr$) and Chantaburi River estuary(mean = 0.20 $g/cm^2/yr$) .

The estimation of Pb-210 age versus depth in core sample from both Bang Pakong and Chantaburi River estuary was calculated and shown in Fig. 8. Such a radiometric dating of sediment core might be a useful tool to evaluate the history and the extent of pollutant contamination recorded in the sediments and may provide a reasonable estimate of natural or background level of the contaminated area, as discussed by Bruland *et al.*[5] and Hamilton-Taylor[6] elsewhere.

CONCLUSION

It can be concluded that Pb-210 radiochronometric method has been successfully applied to the sedimentary column from the Bang Pakong and Chantaburi River Estuary. The sedimentation rates, determined in the core samples, were found to be 0.46-0.69 cm/yr. In general the sedimentation rates of Bang Pakong are higher than those from the Chantaburi River estuary. This probably is due firstly to rapid removal of the mangrove forests of the area and secondly, loss of Pb-210 from deeper sections of sedimentary column from the Bang Pakong River as a result of early diagenetic processes gives the appearance of greater sedimentation.

ACKNOWLEDGEMENTS

The authors would like to express their sincere thanks to the Office of the Atomic Energy for Peace (OAEP), Thailand for their technical assistances in Pb-210 radiometric dating. Many thanks to Professor Ian Brindle for reading this manuscript and valuable suggestions. This work was partially supported by Burapha University Research Fund.

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บทคัดย่อ

ได้เก็บตัวอย่างแท่งตะกอนดินจำนวน 18 แท่งจากบริเวณชะวากทะเล (estuary) บริเวณแม่น้ำบางปะกงและแม่น้ำจันทบุรี. ผลการวิเคราะห์ปริมาณ excess Pb-210 สามารถนำมาใช้ในการคำนวนอัตราการตกตะกอน และอายุชั้นดินในแท่งตะกอนได้เป็นอย่างดี. วิธีการศึกษาอายุชั้นดินจากอัตราการตกตะกอนนี้ใช้สมมุติฐานว่าการนำเข้า (flux) ของ Pb-210ที่เกิดจากการสลายตัวของ Rn-222 จากบรรยากาศ และการดูดซับ Pb-210 บนอนุภาคแขวนลอยที่ตกตะกอนลงในบริเวณชะวากทะเลมีอัตราที่คงที่. ผลการวิจัยยังชี้ให้เห็นว่าอัตราการตกตะกอนบริเวณปากแม่น้ำบางปะกงมีอัตราสูงกว่าปากแม่น้ำจันทบุรี ทั้งนี้อาจเป็นผลเนื่องมาจากการทำลายป่าชายเลนอย่างรวดเร็วในบริเวณปากแม้น้ำบางปะกงเมื่อเปรียบเทียบกับบริเวณแม่น้ำจันทบุรี และเป็นผลเนื่องมาจากขบวนการ diagenesis ของ Pb-210 ในชั้นดินตะกอนที่ลึกลงไปจากผิวดิน.