

## Changes of Phosphorus, $^{210}\text{Po}$ and $^{210}\text{Pb}$ in water column at Mersing River, Johor

(Perubahan fosforus,  $^{210}\text{Po}$  dan  $^{210}\text{Pb}$  dalam turus air di Sungai Mersing, Johor)

<sup>1</sup>Saili, N.A.B., <sup>2</sup>Mohamed, C.A.R.

<sup>1</sup> School of Environmental and Natural Resource Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor

<sup>2</sup> Ecosystem Marine Research Centre (EKOMAR), Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor.

Received 7 May 2012; accepted 7 Oktober 2012

### ABSTRACT

*The studies on natural radionuclides such as  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  with the concentration of phosphorus in water column were carried out in Mersing River, Johor. There were 16 water samples were collected from nine stations during Mersing Expedition 2010 on the 4<sup>th</sup> July 2010. The samples were treated by using sequential extraction and counted using the gross alpha-beta counting system (Tennelec model 5 XLB low background gas-flowing anti-coincidence alpha-beta counter) for  $^{210}\text{Pb}$  and alpha spectrometry counting system (Canberra model Alpha Analyst Spectroscopy system with a silicon-surface barrier detector) for  $^{210}\text{Po}$ . The  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  activities were varied between 0.755 to 2.238 mBq/L and 0.1555-1.598 mBq/L. While the phosphorus concentrations include TDP, SRP and DOP were in the range of 6.058 to 23.312  $\mu\text{g/L}$ , 2.237 to 13.419  $\mu\text{g/L}$  and 0.466 to 16.097  $\mu\text{g/L}$ . Statistically, the activities of  $^{210}\text{Po}$  were positively correlated with TDP. In this study, the highest distribution of phosphorus and  $^{210}\text{Po}$  were found at Station 5 which located at boats jetty and very close to Mersing Town area while  $^{210}\text{Pb}$  was found at Station 1.*

Keywords: Phosphorus,  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ , seawater, river, water column

### ABSTRAK

Kajian mengenai radionuklid semulajadi seperti  $^{210}\text{Po}$  dan  $^{210}\text{Pb}$  terhadap kepekatan fosforus di dalam turus air telah dijalankan di Sungai Mersing, Johor. Sebanyak 16 sampel air telah diambil daripada sembilan stesen semasa Ekspedisi Mersing pada 4 Julai 2010. Sampel telah dianalisis menggunakan kaedah pengekstrakan berturut dan dikira dengan menggunakan system gross alfa beta (Tennelec model 5 XLB low background gas-flowing anti-coincidence alpha-beta counter) untuk  $^{210}\text{Pb}$  manakala  $^{210}\text{Po}$  menggunakan sistem alfa spektrometri (Canberra model Alpha Analyst Spectroscopy system with a silicon-surface barrier detector). Julat aktiviti  $^{210}\text{Po}$  dan  $^{210}\text{Pb}$  masing-masing adalah di antara 0.755 - 2.238 mBq/L dan 0.1555 - 1.598 mBq/L. Manakala kepekatan fosforus termasuk TDP, SRP dan DOP adalah di antara 6.058 - 23.312  $\mu\text{g/L}$ , 2.237 - 13.419  $\mu\text{g/L}$  dan 0.466 - 16.097  $\mu\text{g/L}$ . Statistik menunjukkan aktiviti  $^{210}\text{Po}$  berkorelasi secara positif terhadap TDP. Dalam kajian ini, taburan fosforus dan  $^{210}\text{Po}$  tertinggi didapati di Stesen 5 di mana ia terletak di kawasan jeti bot dan kedudukannya sangat hamper dengan Bandar Mersing manakala  $^{210}\text{Pb}$  didapati Stesen 1.

Katakunci: Fosforus,  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ , laut, sungai, turus air

## INTRODUCTION

Phosphorus, (P) is an essential element utilized by organisms for growth and metabolism and significantly involved in biological productivity in aquatic ecosystem (Hecky and Kilham 1988). The distribution of plankton in marine ecosystem probably influence by P (Benitez-Nelson 2000). Moreover, it plays a critical role in eutrophication of water bodies (Vollenweider 1968, Froelich et al. 1982). It can cause "red tide" problem where the production of toxic by algae bloom due to high concentration of P in marine ecosystem. According to Zhang et al. (2004) most of the study on P focus on the inorganic P in marine ecosystem.

Currently, a few studies of the changes of P, polonium-210, ( $^{210}\text{Po}$ ) and lead-210, ( $^{210}\text{Pb}$ ) had been carried out by researchers from outsider countries. Most of the researches were done at the phosphate mining area and P fertilizer factory due to the P concentrations have a potential increase the rate of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  radioactivity (Carvalho 1995, 1997, Haridson et al. 2001).  $^{210}\text{Po}$  (half-life = 138 days), is an  $\alpha$ -emitter which produced by the decay of  $^{210}\text{Pb}$  (half-life = 22.3 years) with  $\beta$ -emitter radiation are members of the uranium-238, ( $^{238}\text{U}$ ) decay series which can give harm to humans at high activities exposure. However, this unique behavior of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  propose them as oceanographic tracers and intensively utilize to study the physical, biogeochemical processes and determine the sources of the pollutant (Nozaki et al. 1990).

Since Malaysia is surrounded by diverse water bodies, the availability of P naturally or anthropogenic might affect the marine ecosystem and should be consider. Therefore, nine stations at Mersing River had been selected for this research base on human activities which have possibility introduce P in marine ecosystem which are strategic site to study the changes of P concentration,  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  activities in water column. In addition, there are lack of information and data of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in marine ecosystem in Malaysia. Thus, this research significantly propose to study the changes of P (TDP, SRP and DOP),  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  and their relationship to understand their behavior in marine ecosystem for future monitoring and the data might useful for upcoming studies.

## MATERIALS AND METHODS

Mersing River is located nearby of Mersing Town which total drainage area is 232 km<sup>2</sup> to the East toward South China Sea. It is well-known as fish landing area since it depends on fisheries sector. Currently, the development of tourism industry at Mersing Town is increase. There are huge jetty for fish landing and tourism transportation with speed boat and ferry facilities to Tioman Island, Sibu Island and others islands nearby. Besides that, there is palm oil plantation where some of the agricultural estate located close to by the Mersing River side. The sampling had been one on the 4<sup>th</sup> of July 2010 during Mersing Expedition 2010 during the flood tide. Table 1 and Figure 1 show the location of sampling site respectively. Stations 1 to 4 refers to brackish area (1.38-20.75 psu) which located at the upper stream while Station 5 until 9 refer to estuary area (31.20-32.98 psu).

Table 1: Coordinate of sampling site at Mersing River, Johor.

Station	Area	Coordinate	
		Latitude (N)	Longitude (E)
1	Upper stream (1.38 - 20.75 psu)	02° 25.062'	103° 48.436'
2		02° 25.348'	103° 48.694'
3		02° 25.579'	103° 48.996'
4		02° 25.558'	103° 49.559'
5	Estuary (31.2 - 32.98 psu)	02° 25.604'	103° 50.002'
6		02° 26.149'	103° 50.396'
7		02° 26.690'	103° 50.962'
8		02° 27.189'	103° 51.404'
9		02° 28.149'	103° 52.419'

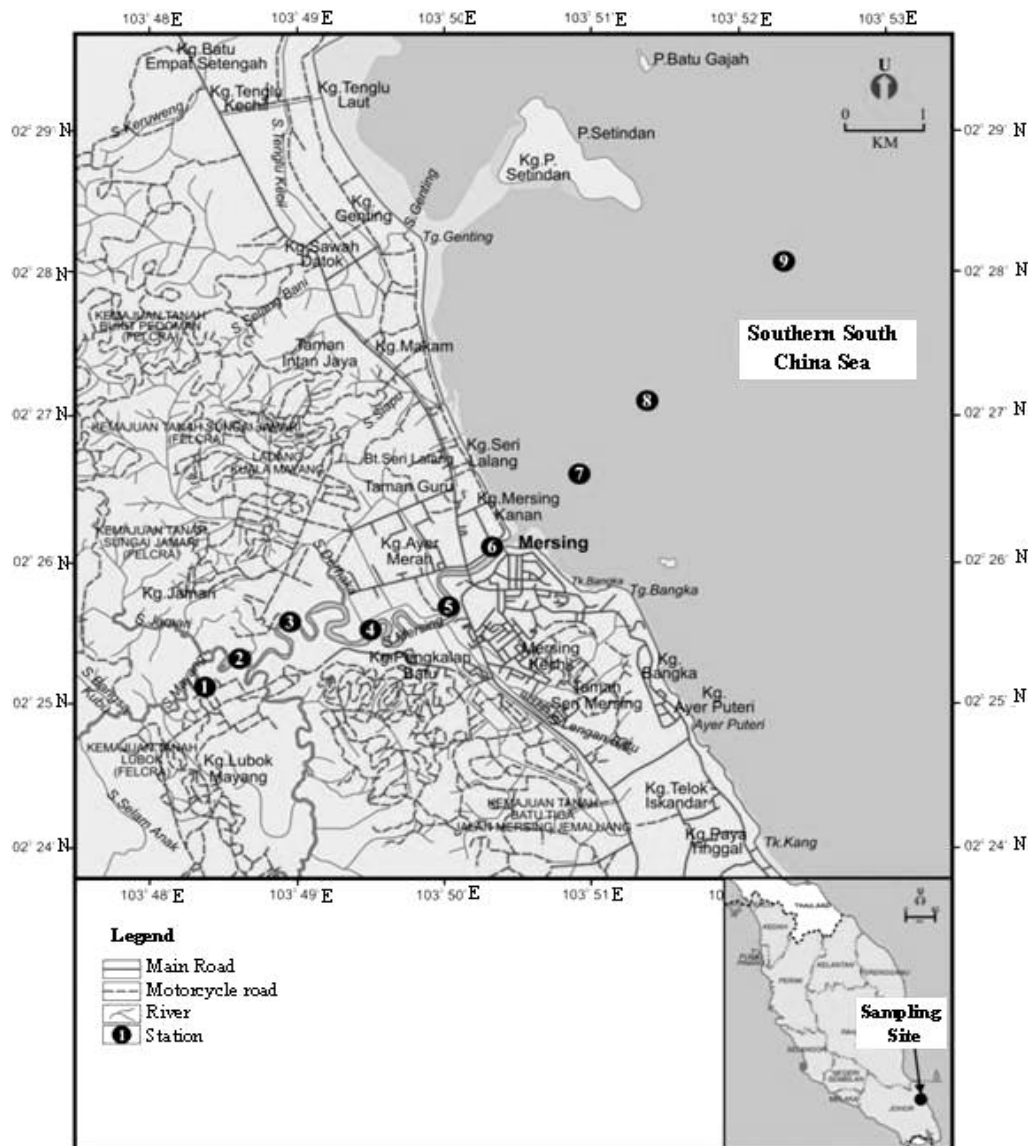


Figure 1: Map of sampling site at Mersing River, Johor.

Soluble reactive phosphorus (SRP) was directly measure by using uv-spectrophotometer. The phosphor-molybdate complex form after 8 minutes react with mixture reagent of ammonium molybdate,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  + sulphuric acid  $\text{H}_2\text{SO}_4$ + potassium antymonitrate,  $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot 0.5\text{H}_2\text{O}$  to ascorbic acid,  $\text{C}_6\text{H}_8\text{O}_6$  at 3:1 ratio. While for the TDP, the samples were run for potassium persulphate,  $\text{K}_2\text{S}_2\text{O}_8$  digestion for 16 hours before measure by using uv-spectrophotometer. The dissolved organic phosphorus (DOP) can be determined from the different between TDP and SRP.

While for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ , the sequential extraction had been utilize. The  $^{210}\text{Po}$  was measured with  $\alpha$ -spectrometer (Canberra model Alpha Analyst Spectroscopy system with a silicon-surface barrier detector) after extraction, radiochemistry purification and spontaneous plating processes. While the  $^{210}\text{Pb}$  counting by using gross  $\alpha/\beta$  counter (Tennelec model Series 5 XLB low background gas-flowing anti-coincidence alpha-beta counter) 30 days after electrodeposited.

## RESULTS AND DISCUSSION

### TDP, SRP and DOP in dissolved phase

The TDP, SRP and DOP are in the range of 6.058 to 23.312  $\mu\text{g/L}$ , 2.237 to 13.419  $\mu\text{g/L}$  and 0.466 to 16.097  $\mu\text{g/L}$ . Figure 2 showed the distribution and the changes of the P (TDP, SRP and DOP) concentration along the Mersing River from upper stream to estuary.

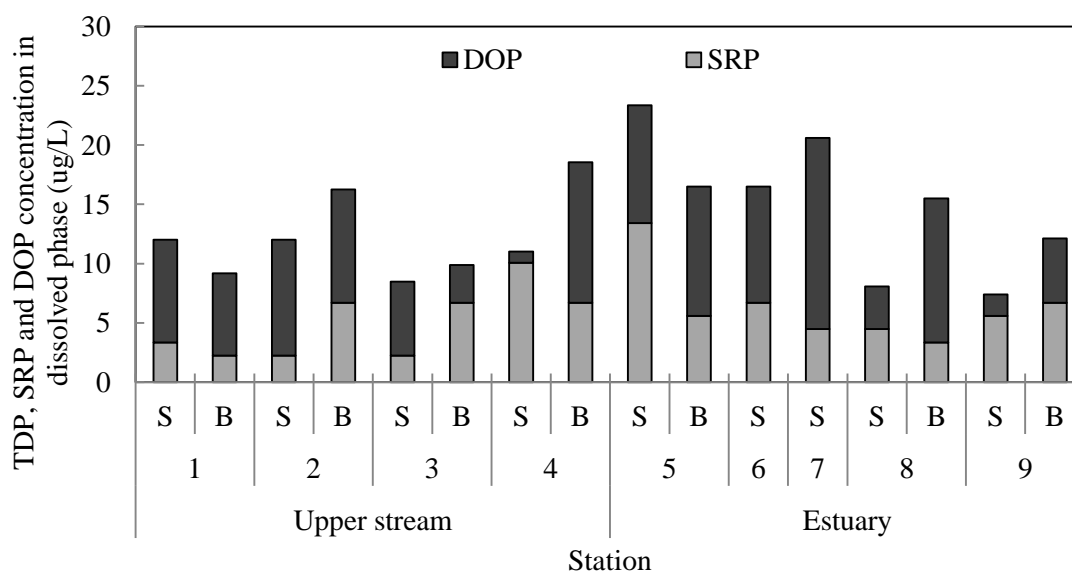


Figure 2: Concentration of P (TDP, SRP and DOP) in dissolved phase of Mersing River, Johor. (S refer to surface, B refer to bottom)

The sampling area had been separating into two region base on salinity regimes which are upper stream and estuary. According to Monbet et al. (2009), sediment is a significant source of potentially P compound in estuary. However, the concentrations of P in sediment are not measure in this study. On the other hand, this study provides evidence that sediment is an important source of P compound by comparison to the relationship between TSM and TDP in the water column which is positively moderate correlation ( $r = 0.686$ )

encouraged from the characteristic of the organic P compound has a strong affinity to particles. Besides, Station 5 which located at jetty where the boat landed shows the highest concentration of P. The boats traffic might cause strong turbulence and contribute the sediment advection from surface sediment of the river. This implies, the organic P associate to TSM which confidentially related to the surface sediment.

**<sup>210</sup>Po and <sup>210</sup>Pb and in dissolved phase**

Figure 4 and Figure 5 show the <sup>210</sup>Po and <sup>210</sup>Pb activities which were varied between 0.755 to 2.238 mBq/L and 0.156-1.598 mBq/L from upper stream to estuary area.

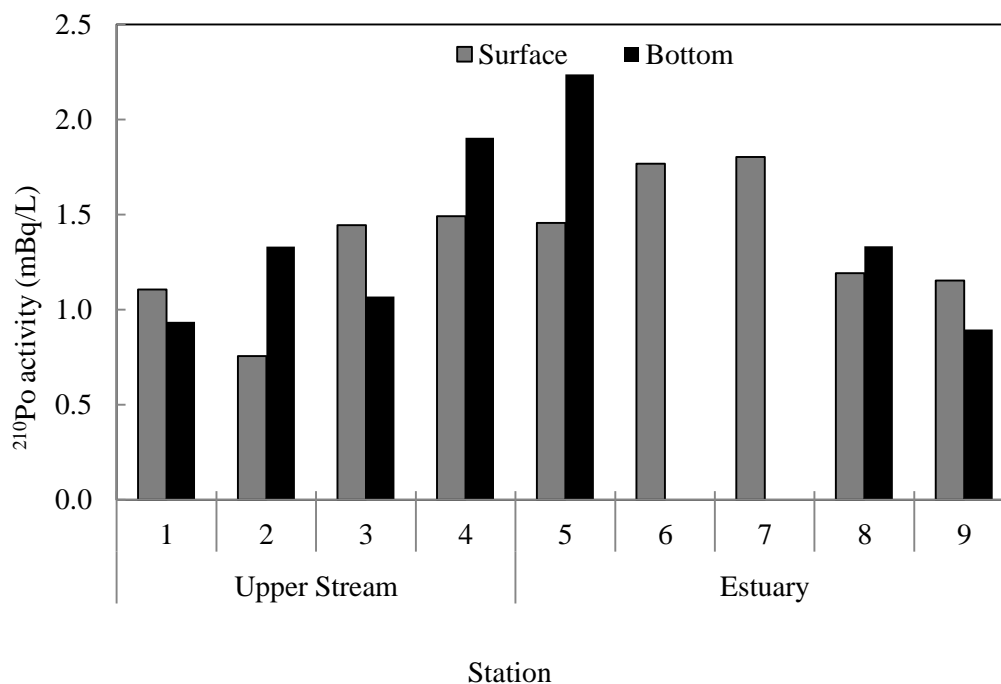


Figure 4: Activities of <sup>210</sup>Po in dissolved phase of Mersing River, Johor.

In this study, the highest activities of <sup>210</sup>Po and <sup>210</sup>Pb were found at Station 5 and Station 1. However, in this study, there is no specific explanation answering the main sources of the radionuclides at each area. Based on the characteristic of each radionuclide, <sup>210</sup>Po generally accumulated in plankton which associated with organic material. In other word, <sup>210</sup>Po has a stronger affinity to particulates compare to its parent, <sup>210</sup>Pb (Gasco et al., 2002). During sampling, the traffic is quite busy at jetty area (Station 5). In other hand, the palm oil agricultural estate located nearby Mersing River. Since the Mersing River is the end point of several rivers, the <sup>210</sup>Po and <sup>210</sup>Pb might introduce into Mersing River by flushing out of waste from these rivers.

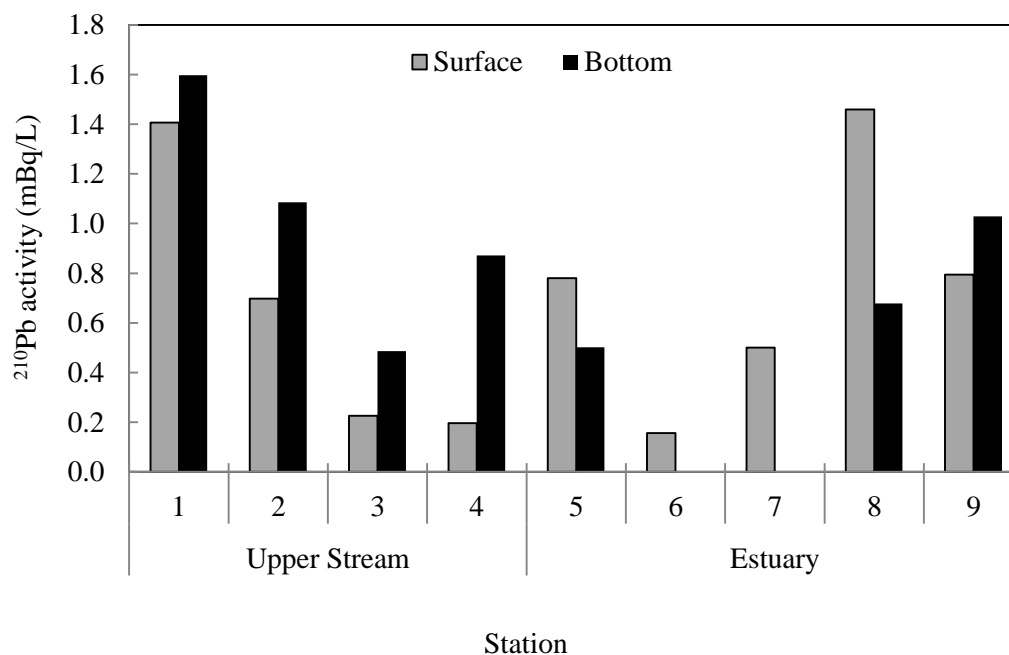


Figure 5: Activities of  $^{210}\text{Pb}$  in dissolved phase of Mersing River, Johor.

The bottom water samples at Station 1 shows the highest activity of  $^{210}\text{Pb}$ . Station 1 is located at the upstream area and the sample has been taken under the bridge where the vehicles pass through every day. Normally  $^{210}\text{Pb}$  introduce into marine ecosystem through deposition of atmospheric input and in situ production by Radium-226,  $^{226}\text{Ra}$  decay (Masque et al. 2002; Yamada & Zheng, 2007). Therefore,  $^{210}\text{Pb}$  sources at Station 1 might origin from vehicles smoke and attach to dust particles before deposited and adsorbed to suspended particulate matter in the river.

#### Relationship of P, $^{210}\text{Po}$ , $^{210}\text{Pb}$ with TSM in water column

Based on the strong affinity to particle characteristic of P,  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ , the statistics correlation,  $r$  are used as an approach to understand the relationship between P,  $^{210}\text{Po}$ ,  $^{210}\text{Pb}$  and TSM in water column. Statistically,  $^{210}\text{Po}$  activity and TSM shows positively high correlation ( $r = 0.847$ ) while  $^{210}\text{Pb}$  activity and TSM shows negatively moderate correlation ( $r = 0.442$ ). This implies that, high possibility of  $^{210}\text{Po}$  sources in the Mersing River are from TSM based on its behavior which is stronger affinity to particulates compare to its parent,  $^{210}\text{Pb}$  (Gasco et al., 2002). While for the  $^{210}\text{Pb}$ , it was suggest that the  $^{210}\text{Pb}$  activity might decay to produce  $^{210}\text{Po}$ .

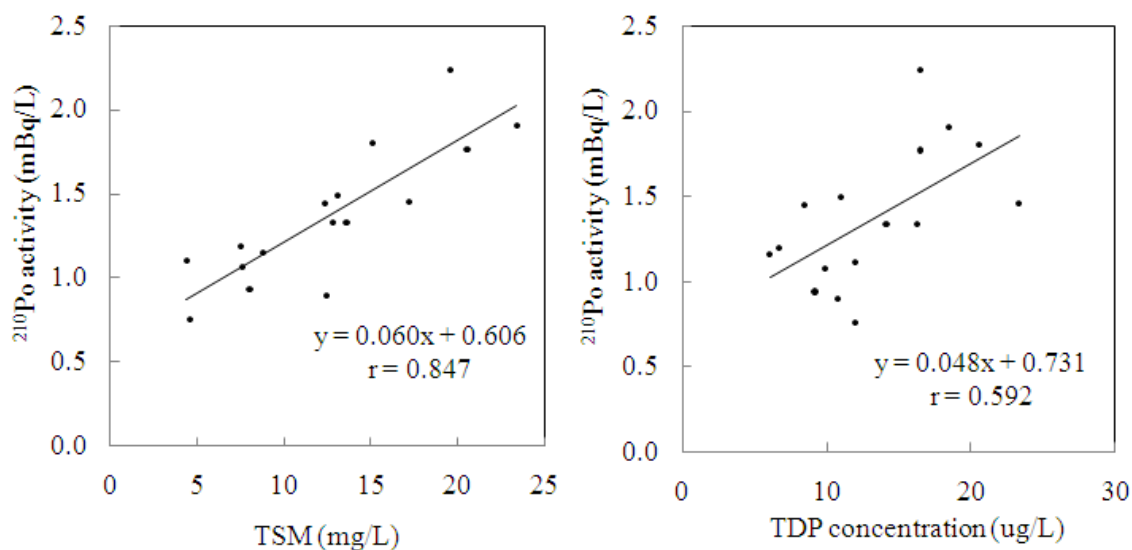


Figure 6: Correlation between <sup>210</sup>Po with TDP and TSM in water column at Mersing River.

Furthermore, <sup>210</sup>Po and TDP in water column shows positively moderate correlation ( $r = 0.592$ ). This indicates that, P concentrations have a potential increase the rate of <sup>210</sup>Po radioactivity (Carvalho 1995, 1997; Haridson et al. 2001).

### CONCLUSION

The <sup>210</sup>Po and <sup>210</sup>Pb activities were varied between 0.755 to 2.238 mBq/L and 0.1555-1.598 mBq/L. While the phosphorus concentrations include TDP, SRP and DOP were in the range of 6.058 to 23.312 µg/L, 2.237 to 13.419 µg/L and 0.466 to 16.097 µg/L. The highest distribution of phosphorus and <sup>210</sup>Po were found at Station 5 which located at jetty and very close to Mersing Town area. The <sup>210</sup>Po and P might introduce into Mersing River from the palm oil agricultural estate waste and human waste from Mersing Town. In others hand, the boats traffic might cause strong turbulence and contribute the sediment advection from surface sediment of the river. The highest <sup>210</sup>Pb was found at Station 1 which is at upstream area, under the bridge where the vehicles pass through every day. Therefore, <sup>210</sup>Pb sources at Station 1 might origin from vehicles smoke and attach to dust particles before deposited and adsorbed to suspended particulate matter in the river. P concentrations have a potential increase the rate of <sup>210</sup>Po radioactivity based on <sup>210</sup>Po and TDP relationship in water column shows positively moderate correlation.

### ACKNOWLEDGEMENTS

Authors would like to thank the organizers of Mersing Scientific Expedition 2010, Marine Ecosystem Centre (EKOMAR). A lot of appreciation to the members of Forestry Agency and Land-Atmospheric-Ocean Interaction (LAOI) Research Group in UniversitiKebangsaan Malaysia (UKM) . This research had been supported by the Ministry of Science, Technology and Innovation (MOSTI), under National Oceanography Directorate (NOD) grant, NOD/R&R/01/002 and National Science Fund (NSF) scholarship, L6438.

## REFERENCES

- Benitez-Nelson, C.R., 2000. The biogeochemical cycling of phosphorus in marine systems. *Earth Science Reviews* **51**, 109-135.
- Carvalho, F.P., 1995.  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in sediment and suspended matter in the Tagus estuary. Local enhancement of natural levels by wastes from phosphate ore processing industry. *Science of Total Environment* **159**, 201-161.
- Carvalho, F.P., 1997. Distribution, cycling and mean residence time of  $^{226}\text{Ra}$ ,  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in Tagus estuary. *Science of Total Environment* **196**, 151-161.
- Froelich, P., Bender, M.L., Luedtke, N.A., Heath, G.R., DeVries, T., 1982. The marine phosphorus cycle. *Am. J. Sci.* **282**, 474-511.
- Gasco, C.A., Anton, M.P., Delfanti, R., Gonzalez, A.M., Mirel, J., Papucci, C., 2002. Variation of the activity concentrations and fluxes of natural ( $^{210}\text{Po}$ ,  $^{210}\text{Pb}$ ) and anthropogenic ( $^{239,234}\text{Pu}$ ,  $^{137}\text{Cs}$ ) radionuclides in Strait of Gibraltar (Spain). *Journal of Environmental Radioactivity* **62**, 241-262.
- Haridson, P.P., Paul, A.C., Desai, M.V.M., 2001. Natural radionuclides in the aquatic environment of a phosphogypsum disposal area. *Environmental Radioactivity* **53**, 155-165.
- Hecky, R.E., Kilham, P., 1988. Nutrient limitation of phytoplankton in freshwater and marine environments: a review of recent evidences of the effects of enrichment. *Limnol.Oceanogr* **33**, 796-822.
- Kim, Y.I., Narita, H., Noriki, S., Tsunogai, S., 1997. Export of Particulate Matter from Tokyo Bay Studied with Radiochemical Tracers,  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ . *Journal of Oceanography* **53**, 517-527.
- Monbet, P., McKelvin, I.D., Worsfold, P.J., 2009. Dissolved organic phosphorus speciation in the waters of the Tamar estuary (SW England). *Geochim.Cosmochim. Acta.* **73**, 1027-1038.
- Nozaki, Y., Ikuta, N., Yashima, M., 1990. Unusually large  $^{210}\text{Pb}$  deficiencies relative to  $^{210}\text{Po}$  in the Kuroshio Current of the East China and Philippine seas. *Journal of Geophysical Research* **95**, 5321-5329.
- Vollenweider, R.A. 1968. *Scientific Fundamentals of the Eutrophication of Lakes and Flowing Waters, with Particular Reference to Nitrogen and Phosphorus as Factors in Eutrophication*. OECD, Paris.
- Yamada, M., Zheng, J., 2007.  $^{210}\text{Pb}$  and  $^{230}\text{Th}$  in settling particles in the western Northwest Pacific Ocean: Particle flux and scavenging. *Continental Shelf Research* **27**, 1629-1642.
- Zhang, Y.S., Zhu, L., Zeng, X., Lin, Y., 2004. The biogeochemical cycling of phosphorus in the upper ocean of the East China Sea. *Estuarine Coastal and Shelf Science* **60**, 369-379.