Asian Journal of Chemistry; Vol. 30, No. 3 (2018), 579-584

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2018.21013

Assessment of Trace Metals Distribution in Lake Kenyir, Malaysia

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Received: 31 August 2017; *Accepted*: 20 December 2017; *Published online*: 31 January 2018; AJC-18748

Measurements of dissolved and particulate trace metals (Cd, Cu, Pb, Fe and Zn) were made on water samples collected from Lake Kenyir, Malaysia. Samples were taken monthly from the same stations during August-October 2010. Comparison with the National Water Quality Standards (NWQS), Malaysia showed that all dissolved trace metals were classified as Class I (clean status) for all surface waters, although some of the trace metals displayed slightly higher concentrations at the eastern part of the lake. No comparison based on NWQS could be made for particulate trace metals as they are not listed in this classification. When comparing with other selected lakes in Malaysia, the trace metals in this study area were among the lowest concentrations.

Keywords: Trace metals, Anthropogenic activities, Malaysian National Water Quality Standard, Lake Kenyir.

INTRODUCTION

Some trace metals are essential elements for living organisms and therefore play many critical roles in the biogeochemical functioning of aquatic systems [1]. For example, cadmium and zinc are fundamental in silica uptake by diatoms, copper and nickel in organic nitrogen utilization and manganese, iron, copper and zinc are essential active structural factors in enzymes [1,2]. Although lead is not an essential micronutrient, it is a major concern owing to its toxicity in aquatic systems [3]. In natural environments, these bio-essential trace metals are usually present in aquatic systems at low concentrations and are important to the living organisms at a 'natural' level, but in excess, they become toxic.

Although trace metals are natural components in a lake, human activities have greatly contributed to their elevated concentration in lake waters. In most of the circumstances, lakes potentially receive anthropogenic sources of trace metals from mining activity, industrial development (*e.g.* smelting activities), waste water discharge containing toxic metals, agricultural run-off of trace metal-containing fertilizers and pesticides and air pollution deposition [4,5]. Once released into environment, anthropogenic trace metals may be of major concern because of their potential toxicity, persistence within environmental settings, possible bioaccumulation in biota and distribution along the food chain [4-6].

Lake Kenyir, the largest man-made lake in South East Asia, was formed to supply the Sultan Mahmud Hydroelectric Power Plant. The lake is surrounded by more than 40 rivers and streams and one of the world's oldest tropical forests, making the lake and its surroundings home to an incredibly diverse array of flora and fauna [7,8]. While being a popular ecotourism destination, with thousands of people visiting each year to take part in activities such as recreation fishing and camping, Lake Kenyir also serves as a commercial fishing ground and fish production park (cage culture). The Como River in Lake Kenyir, which is a large-scale Aquaculture Industrial Zone (AIZ), has been given priority for fish culture since 2005 and the cage culture production in 2012 was predicted to produce as much as 10,000 tons [9]. In the lake, at least 60 fish species are known to occur [8], with 36 species caught for commercial purposes and a yield of 1.3-20.0 kg ha^{-1} yr^{-1} fish production [10]. Being an important ecotourism destination and fish production area, in addition to the on-going development programs to utilize the lake, the level, distribution and sources of these trace metals in Lake Kenyir can be helpful in identifying water quality and have wide implications for the social, economic and human health of the region, as well being an important issue within the context of the management of lake.

This paper reports the levels of Cd, Cu, Pb, Fe and Zn in dissolved and particulate phases in Lake Kenyir and in addition provides a fundamental information on their distribution, as well as discusses known and likely processes controlling their concentration on a spatial basis. Results obtained for these trace metals were also compared with Malaysian National Water Quality Standards (NWQS) as listed in Table-1, to determine the suitability of this water body for its users [11].

EXPERIMENTAL

Lake Kenyir is located in Terengganu on the east coast of Peninsular Malaysia (Fig. 1). The 32 sampling stations cover the eastern part of the Lake Kenyir (ELK: stations K1 to K15) and Terengganu National Park (TNP: stations N1 to N17). Water samples were collected monthly during the dry season from August to October 2010, using a Van Dorn sampler for the measurement of both dissolved and particulate trace metals. Water samples were collected from both surface and deeper layers (*i.e.* 30 m below the surface) at the ELK stations, but only surface waters were collected for TNP stations due to their shallow waters. Upon collection, samples were stored in an icebox with ice and then transported to the laboratory.

At the laboratory, the water samples were filtered through acid-cleaned 0.45 µm membrane filters in a laminar flow hood (class 100). The filtrate for the dissolved phase analysis was acidified to pH < 2 by the addition of analytical grade nitric acid after transfer to acid-washed high-density polyethylene bottles, while the filters which contained the suspended particulate material were processed for particulate trace metal analysis. Water samples for dissolved trace metals (Cd, Cu, Pb, Fe and Zn) were then extracted, pre-concentrated and the matrix removed using the ammonium pyrrolidine dithiocarbamate into methyl isobutyl ketone solvent extraction method according to Magnusson & Westerlund [12]. Finally, concentrations of these trace metals were determined by graphite furnace atomic absorption spectrophotometry (GFAAS).For particulate trace metals, the filtered suspended particulates were digested in Teflon vessels for 7 h at 100 ºC in a mixture of HNO_3/HCl/HF (3:3:1.5). After cooling, the digested solutions were diluted with deionized water in the presence of boric acid, in order to remove HF [13]. Particulate trace metal concentrations were lastly measured by inductively coupled plasma optical emission spectroscopy (ICP-OES). To evaluate the performance of the analytical procedures two metal solutions, containing 5 µg/L and 10 µg/L of Cd, Cu, Pb, Fe and Zn respectively, were pre-concentrated and analyzed with the samples. The recoveries of known concentration of metal solutions ranged from 80 to 92 %.

RESULTS AND DISCUSSION

Spatial distribution: The trace metal data are presented as mean concentrations from the 3 month sampling period and plotted in the respective figures. Fig. 2 shows the dissolved trace metal (Cd, Cu, Pb, Fe and Zn) concentrations along the ELK and TNP transects. The concentrations from the ELK transect (stations K1-K15) were in the ranges 0.113-0.247 (0.196 ± 0.041) µg/L Cd, 0.391-1.521 (0.814 ± 0.332) µg/L Cu, 0.183-1.082 (0.599 ± 0.287) µg/L Pb, 4.93-13.83 (8.92 ± 2.37) µg/L Fe and 8.13-37.03 (15.16 ± 8.05) Zn, while for the TNP transect they varied in the ranges 0.269-0.388 (0.339 ± 0.033) µg/L Cd, 0.154-0.320 (0.217 ± 0.047) µg/L Cu, 0.278-0.573 (0.395 ± 0.082) µg/L Pb, 0.075-3.350 (1.206 ± 0.879) µg/L Fe and 13.55-26.28 (19.09 ± 3.80) µg/L Zn. The relative order of concentrations was Zn > Fe > Cu > Pb > Cd for the ELK transect and Zn > Fe > Pb > Cd > Cu for TNP. Levels of trace metals in the lake waters for both the ELK and TNP transects were generally low with moderate variations and within the ranges of Class I based on the Malaysian National Water Quality Standards (NWQS) classification, considered the natural background level with respect to metals (Table-1). This is especially true for the sampling transect of TNP which serves as a protected national park area with minimum disturbance from human activity.

Although the concentrations of trace metals at the sampling sites were low, they still varied spatially, in which transect 1 (stations K1 to K10) generally had higher trace metal concentrations than transect 2 (stations K11-K15) and TNP. For example, slightly higher concentrations of trace metals were observed in the northern part of transect 1 (stations K7, K8, K9 and K10), which is close to Pangkalan Gawi, which serves as a jetty and is an area with lakeside restaurants and homesteads and the concentrations gradually decreased south of transect 1. This result suggests that importance of anthropogenic inputs from the jetty, lakeside restaurants and homesteads in elevating the trace metal concentrations at these stations. Studies have shown most of the trace metals sources were anthropogenic; for example, Pb could be related to automobile exhausts [14], Cu

TABLE-1
NATIONAL WATER QUALITY STANDARDS FOR MALAYSIA [Ref. 11]

Parameter	Unit	Class				
		I	IIA/IIB	III#	IV	V
Cd	mg/L	Natural level or absent	0.01	0.01* (0.001)	0.01	Level above IV
Cu	mg/L	Natural level or absent	0.02	–	–	Level above IV
Pb	mg/L	Natural level or absent	0.05	0.02* (0.01)	5	Level above IV
Fe	mg/L	Natural level or absent	1.00	1	5	Level above IV
Zn	mg/L	Natural level or absent	5.00	0.4*	2	Level above IV

*At hardness 50 mg/L $CaCO_3$; #Maximum (unbracketed) and 24 h average (bracketed) concentrations

Classes	Uses
Class I	Conservation of natural environment
	Water supply I – Practically no treatment necessary
	Fishery I – Very sensitive aquatic species
Class IIA	Water supply II – Conventional treatment required
	Fishery II – Sensitive aquatic species
Class IIB	Recreational use with body contact
Class III	Water supply III – Extensive treatment required
	Fishery III – Common of economic value and tolerant species; livestock drinking
Class IV	Irrigation
Class V	None of the above

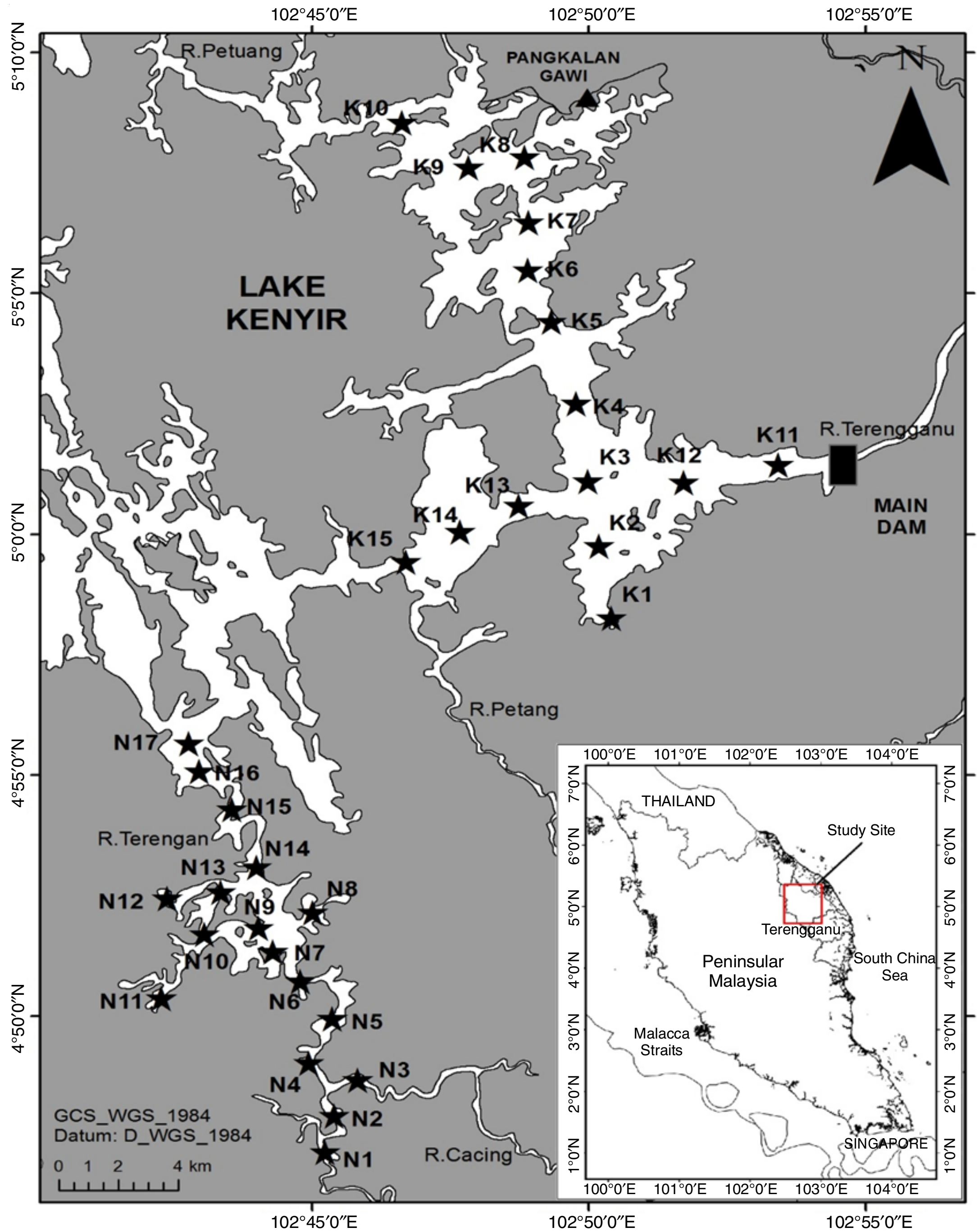

Fig. 1. Sampling stations in Lake Kenyir

might originate from paint used on boats and sewage inputs [15] and elevated Fe and Cd concentrations are often found near major urban centres and in urban waste-water [16,17].

The concentrations of particulate trace metals in ELK and TNP are presented in Fig. 3. Their relative orders of concentrations were Fe > Zn > Pb > Cd > Cu and Fe > Cd > Cu > Zn > Pb for ELK and TNP, respectively. Across the ELK transect, the concentrations of particulate trace metals were 0.013-0.017 (0.016 ± 0.001) mg/L Cd, 0.008-0.0200 (0.015 ± 0.003) mg/L Cu, 0.036-0.079 (0.059 ± 0.010) mg/L Pb, 20.26-37.97 mg/L (28.61 ± 4.27) mg/L Fe and 2.93-5.03 (4.35 ± 0.55) mg/L Zn. Again, the TNP transect generally showed lower trace metal concentrations of 0.024-0.027 (0.027 ± 0.001) mg/L Cd, 0.006-0.013 (0.010 ± 0.003) mg/L Cu, 0.001-0.007 (0.003 ± 0.002) mg/L Pb, 3.05-6.39 (5.84 ± 0.94) mg/L Fe and 0.004-0.025 (0.012 ± 0.007) mg/L Zn. Unfortunately, particulate trace metals are not listed in the NWQS classification to determine the suitability of the water body to its users, therefore there is no comparison based on this standard to be made.

The vertical distributions of dissolved and particulate trace metals are presented in Figs. 2 and 3, respectively. Vertical profiles of Zn and Fe showed surface depletion in dissolved form and bottom enrichment in particulate form, suggesting that dissolved Zn and Fe were removed from the surface waters and transported to the deeper waters *via* biological and/or physico-chemical pathways [16,18]. However, surface layer enrichment and deeper layer depletion was observed in the case of Cd and Cu profiles, unlike their normal distribution,

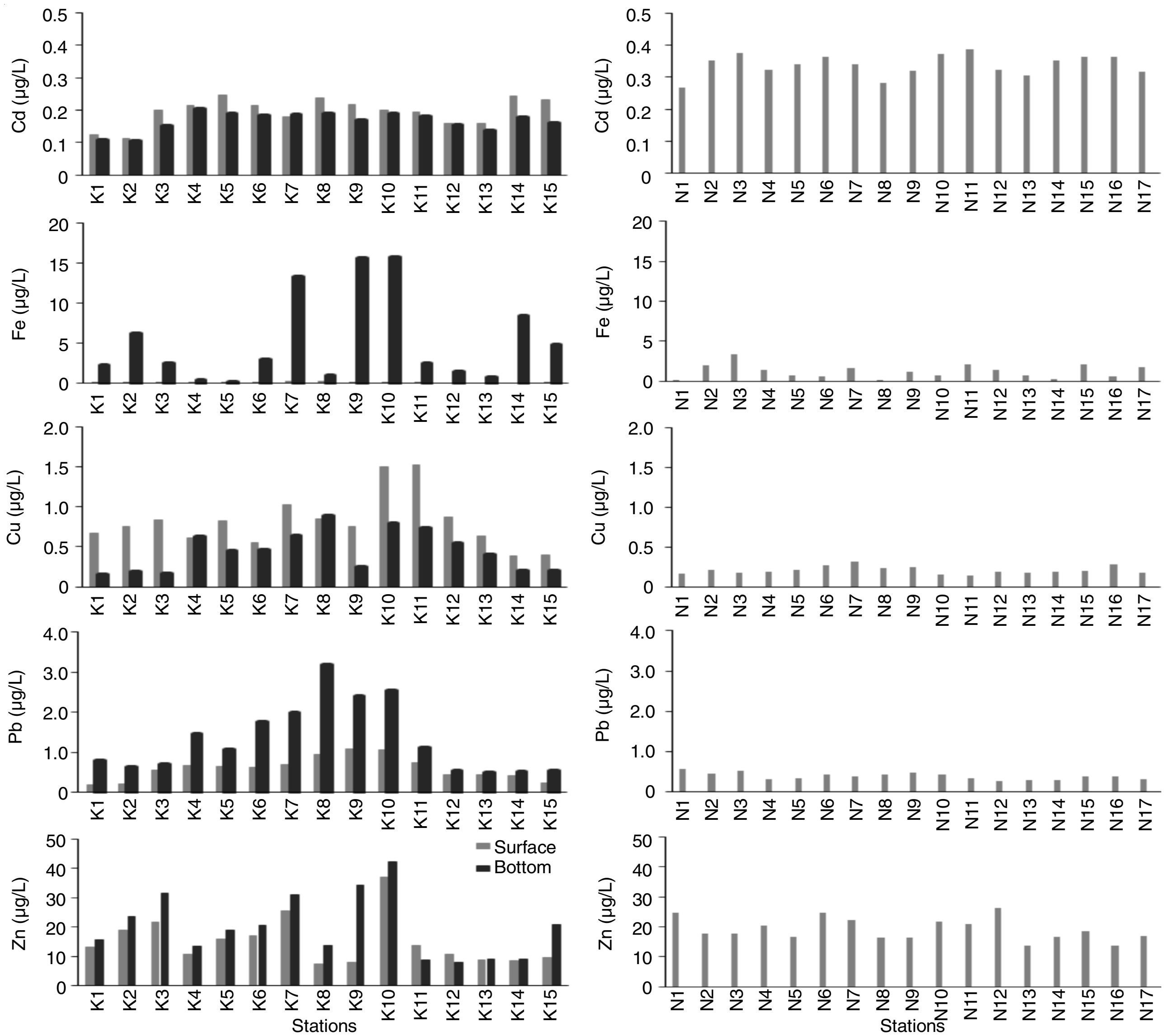

Fig. 2. Variation of dissolved trace metals in Lake Kenyir

probably as a result of anthropogenic sources and riverine input to the surface waters. Dissolved Cu did not show any depletion in the surface waters. This could be due to strong organic complexation which would reduce the inorganic free Cu^{2+} pool that is directly available for biological uptake [19]. Vertical distributions of Pb indicated relatively lower concentrations in the surface layer with increases at the deeper layer, suggesting scavenging of Pb from solution onto particles and less efficient atmospheric input in this study area [19].

Comparison with some selected previous studies in Malaysia: The concentrations of Cd, Cu, Pb, Fe and Zn in this study were compared with some selected previous studies in the lakes of Malaysia (Table-2). Unfortunately, these previous studies focused mainly on the dissolved form of trace metals, therefore, only dissolved trace metals were used for comparison in Table-2.

Trace metals in Lake Kenyir and tropical hydroelectric reservoir [20] fell into Class I of the NWQS, which indicates a natural level of trace metals in their water bodies. For Lakes Sembrong [21] and Chini [22], some of the trace metal concentrations (*i.e.* Cu in Lake Chini; Cu, Pb in Lake Sembrong) in the water column lay between the boundary of Class I and II. Even worse, the concentrations of Fe in Lake Sembrong fell on the boundary of Class II and III. Overall, Lake Sembrong had the highest mean concentrations for all the trace metals involved in comparison, while Lake Kenyir had the lowest of all trace metal concentrations. The slightly polluted Lake Sembrong was explained in their study by additional sources potentially derived from anthropogenic inputs such as the application of pesticides and inorganic fertilizers, as well as atmospheric deposition, particularly from the catchment area. Meanwhile, it is not surprising that the Lake Kenyir had among the lowest concentrations of trace metals in its water column as it is a protected national park area, although there are some on-going development programs mainly to utilize the lake. Therefore, it is important to have well-established management and regular monitoring programs in Lake Kenyir in order to maintain its good water quality.

Conclusion

The low levels of trace metals in Lake Kenyir, which fell within Class I in the NWQS classification, reflect the good

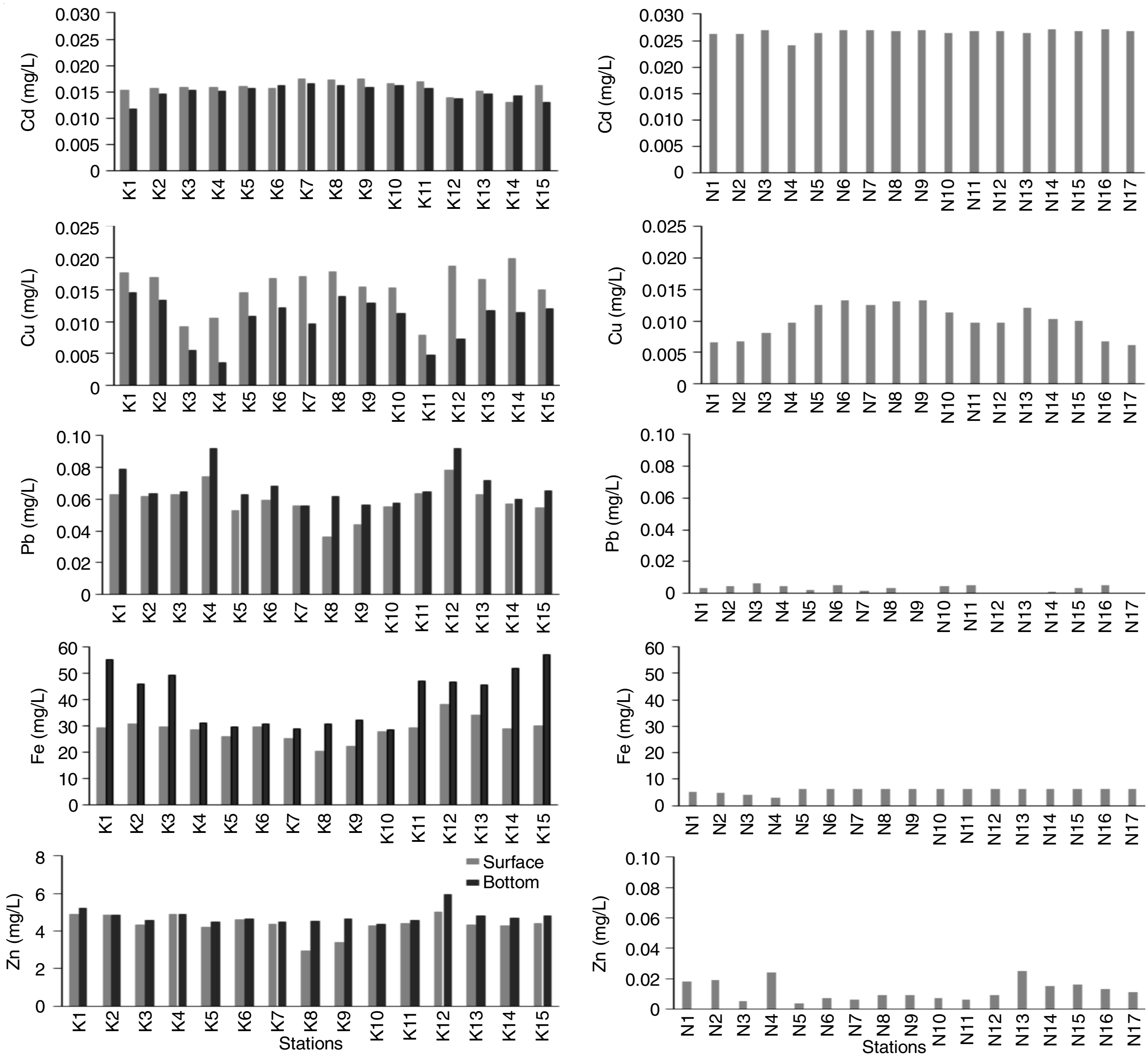

Fig. 3. Variation of particulate trace metals in Lake Kenyir

TABLE-2
COMPARISON OF TRACE METALS WITHIN SELECTED STUDY AREAS

Location	Dissolved (μg/L)					Ref.
	Cd	Cu	Pb	Fe	Zn	
Lake Kenyir, Terengganu	0.113-0.388 (0.272)	0.154-1.521 (0.497)	0.183-1.082 (0.491)	0.075-13.83 (4.82)	8.13-37.03 (17.25)	Present study
Lake Sembrong, Johor	–	0-33 (6.47)	0.002-11 (3.05)	371-3757 (744)	3-270 (46)	[21]
Tropical Hydroelectric Reservoir, Sarawak	–	-	-	(251) ± 179	ND	[20]
Lake Chini, Pahang	0.01-1.04 (0.11)	0.75-26.36 (3.79)	1.70-57.00 (7.54)	-	-	[22]

ND = not detected; ( ) = mean

water quality of the lake. However, the spatial distribution of dissolved trace metals still indicated that they might be related to anthropogenic inputs from the jetty and other anthropogenic activities at Pangkalan Gawi. In comparison with other selected lakes in Malaysia, Lake Kenyir had among the lowest concentrations of trace metals in its surface layer, due to its status as a protected national park. However, there are on-going development programme to utilize the lake. Therefore, effective management and regular monitoring of Lake Kenyir are important in order to maintain its natural background level with respect to trace metals.

ACKNOWLEDGEMENTS

This study was partially supported by Ministry of Education, Malaysia (Fundamental Research Grant Vote No. 59313). The assistance of Miss Yan Xin Huiin the sampling and analysis is kindly acknowledged. Thanks to Dr. Rose Norman for assistance with proof reading of the manuscript.

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