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Trend in metals variation in Tasik Chini, Pahang, Peninsular Malaysia

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Abstract Water from 15 sampling stations in Tasik Chini (Chini Lake), Peninsular Malaysia were sampled for 12months from September 2004 until August 2005 and analyzed for 11 metals including iron (Fe), aluminum (Al), manganese (Mn), barium (Ba), zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd), nickel (Ni), chromium (Cr) and cobalt (Co). Results showed that the mean (min–max) metal concentrations (in micrograms per liter) in Tasik Chini waters for the 12months sampling based on 15 sampling stations (in descending order) for Fe, Al, Mn, Ba, Zn, Pb, Cu and Cd were 794.84 (309.33–1609.07), 194.53 (62.37–665.93), 29.16 (16.68–79.85), 22.07 (15.64–29.71), 5.12 (2.224–6.553), 2.36 (1.165–4.240), 0.832 (0.362–1.443) and 0.421 (0.254–0.696) respectively. Concentration for three metals i.e. Ni, Cr and Co were too low and not detected by the graphite furnace Atomic Absorption Spectrophotometry (AAS). Comparison with various water quality standards showed that the mean metals concentration in surface water of Tasik Chini were low and within the range of natural background except for Fe and Al. In general, metal concentrations in Tasik Chini water varied temporally and spatially. The main factors influencing these metal concentrations in the water were the raining season and mining activities. Stations located at Tanjung Jerangking and Melai areas were the most effected due to those factors.

Keywords Tasik Chini · Peninsular Malaysia · Heavy metal · Natural lake · Water quality

Introduction

Agricultural, logging, mining and other human activities within the Tasik Chini basin, can result in pollution by a variety of contaminants and subsequent degradation of ecosystem health. Metals as one of the main pollutant, can be a threat to the lake ecosystem. Under certain environmental conditions metals may accumulate to toxic concentration and cause ecological damages (Freedman 1989). The major sources of metal pollution in marine and freshwater systems come from domestic wastewater effluents (especially As, Cr, Cu, Mn and Ni), coal-burning power plants (especially As, Hg and Se), non-ferrous metal smelters (Cd, Ni, Pb and Se), iron and steel plants (Cr, Mo, Sb and Zn) and dumping of sewage sludge (As, Mn and Pb; Nriagu and Pacyna 1988). Data on metal contamination in a natural environment (lake or

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river) could be very useful. Information on the occurrence (spatial and temporal distribution) of metals in the ecosystem further understanding of the role human activities play in discharging these chemical to the environment. These useful information serve as a benchmark for assessing contaminant discharge-reduction strategies (Marvin et al. 2004). The assessment of metal contamination in the field can provide information on this metal's availability and describe adverse effects in organisms and is therefore of great significance as a tool for environmental management and conservation. Concentration–response information developed under controlled laboratory conditions can be compared with predicted or measured concentrations in the environment and estimates of relative risk can be made (Graney et al. 1995).

Tasik Chini is the second largest natural lake in Peninsular Malaysia, located in the state of Pahang. The lake plays an important role as a natural wetland ecosystem as its presence reduces the frequency, level and velocity of floods and riverbank erosion. Other significant roles provided by the lake include the fish source for the local community, basic facility for the livelihood and as a mean of the transportation (boating). In recent years, the hinterland of Tasik Chini experienced major development in agriculture and other activities such as building of infrastructure for the National Service Centre situated close to the lake riparian zone and re-activation of iron mine. Large areas of forest conversion to oil palm plantation and illegal logging activities have contributed to the lost of forest area and land degradation. Since Tasik Chini flows to the main river, Pahang River, it is very much influence by the intertidal monsoon season. The strong river current from Pahang River which surge into the lake through Chini River (Fig. 1) during the high monsoon season brings in high loading of suspended solids and other contaminants such as ammonia-N (Shuhaimi-Othman et al. 2007). Therefore it is important that a study is conducted to assess the trend of metal changes in the lake during the seasons and to develop an effective sustainable management and conservation strategies.

This study was conducted for the duration of 12months, which began in September 2004 and ended in August 2005. A total of 11 metals were measured in surface water of the lake. The aim of this study is to determine the changes of metals concentration in the Tasik Chini within 12 months in association to the seasonal variation and other activities occurring within the lake vicinity.

Materials and methods

Study area and sampling stations

Tasik Chini is made up of a series of 12 lakes or opened water body recognized as 'seas' by local residents. The 12 'seas' are Gumum, Pulau Balai, Cenahan, Tanjung Jerangking, Genting Teratai, Mempitih, Kenawar, Serodong, Melai, Batu Busuk, Labuh and Jemberau (Fig. 1). In the present study, 15 sampling stations (1–15) were selected to cover all areas of the lake (Fig. 1) and the GPS position for each sampling station and the detail background of the study areas are described in Shuhaimi-Othman et al. (2007).

Sampling

Field sampling was conducted monthly which began from September 2004 to August 2005. Surface water was collected from each station (three replicates) in HDPE bottle 60ml after acidification to pH < 2 with Aristar® nitric acid (70%) to minimizes the absorption of metals into the wall of the containers and later stored approximately at 4°C. Metal analysis in all samples was carried out by Inductively Coupled Plasma-Optical Emission Spectrophotometry (ICP-OES, model Perkin-Elmer OPTIMA 4300) and graphite furnace Atomic Absorption Spectrophotometry (GFAAS -model Perkin-Elmer AAnalyst 800). Eleven metals were analysed in water samples i.e. iron (Fe), aluminum (Al), manganese (Mn), barium (Ba), zinc (Zn), lead (Pb), copper (Cu), cadmium (Cd), nickel (Ni), chromium (Cr) and cobalt (Co). For GFAAS and ICP-OES, standard and blank samples were analysed every 20 samples. Water hardness samples (Ca^{+2} and Mg^{+2}) were fixed with Aristar® nitric acid (70%) and measured by flame Atomic Absorption Spectrophotometry (AAS).

In-situ parameters

Three replicates of the chemical and physical variables of the lake water were measured directly at each

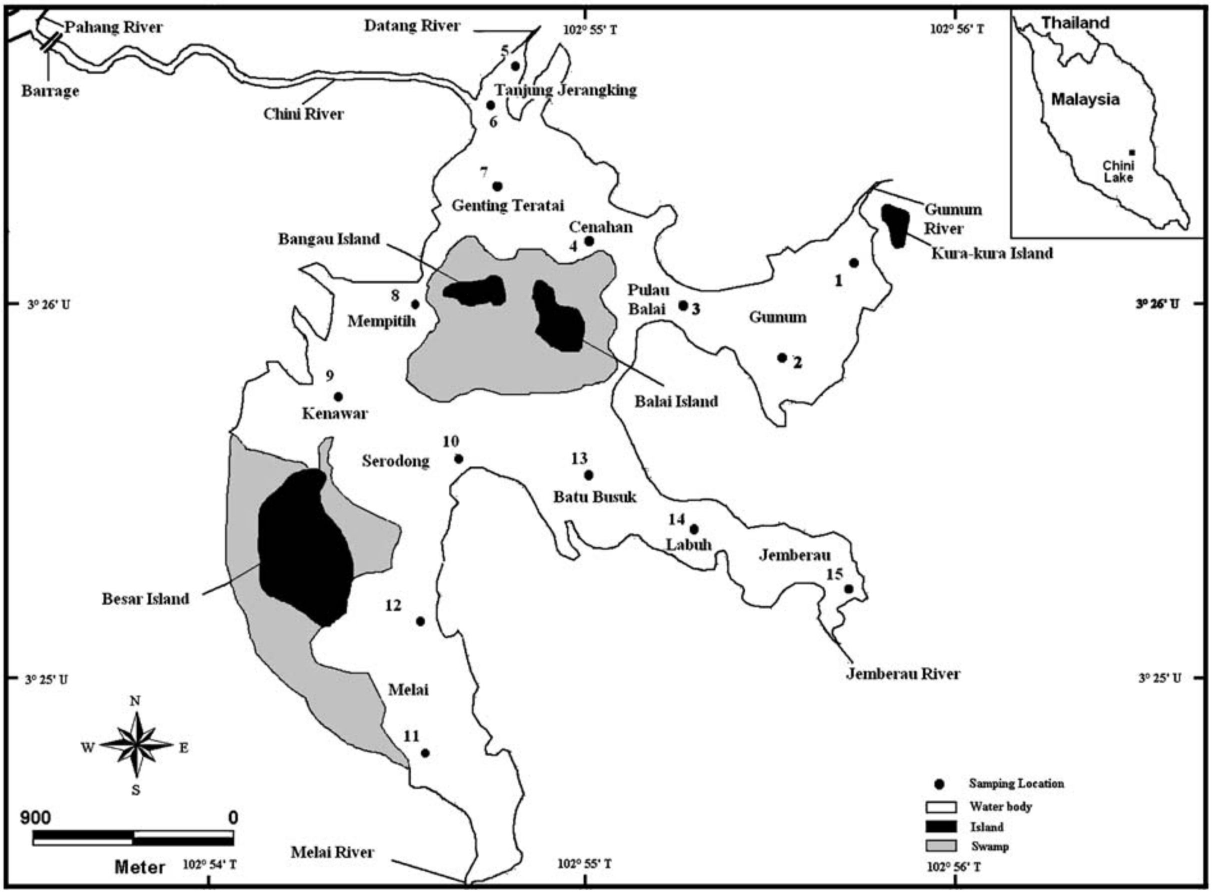

Fig. 1 Location of Tasik Chini and the sampling stations

sampling station using HYDROLAB DataSonde® 4 and Surveyer® 4a. These were temperature, dissolved oxygen (DO), conductivity, pH and total dissolved solid (TDS) concentration. Calibration of every HYDROLAB DataSonde® 4 probes was conducted in the laboratory before field sampling.

Statistical analysis

Statistical analysis was conducted by one-way ANOVA and Tukey–Kramer multiple comparison tests. Data were tested for normality (Shapiro–Wilk test) and homogeneity (Barlett's χ^2) and to meet these requirements, data were transferred to log10. Data that did not meet the requirement (non-parametric data) were tested with Kruskal–Wallis and Mood's median test. Correlation analyses (Pearson) were used to test the relationship between rainfall, chemical and physical variables with heavy metals concentration in the water. Because of the large number of correlation run ($n = 180$), several of these will be expected to come up significant by chance alone. Hence, only the ones at $p < 0.001$ should be accepted as "truly significant" and the others ($p < 0.01$ and $p < 0.05$) should be viewed as possibly significant relationships. Trend analysis (linear trend) were used to analyse the data and fitted in the graph to examine the trend changes for each metal and physical chemical parameters. All data were analysed using statistical package Minitab (vers. 13).

Results and discussion

The rainfall through the sampling period was acquired from Malaysian Meteorological Centre (MMS; Fig. 2). Rainfall data was based on readings at a town in Felda Chini Dua situated about 10km from Tasik Chini. From September 2004 to August 2005, the rainfall recorded in Tasik Chini was 2,108.2mm

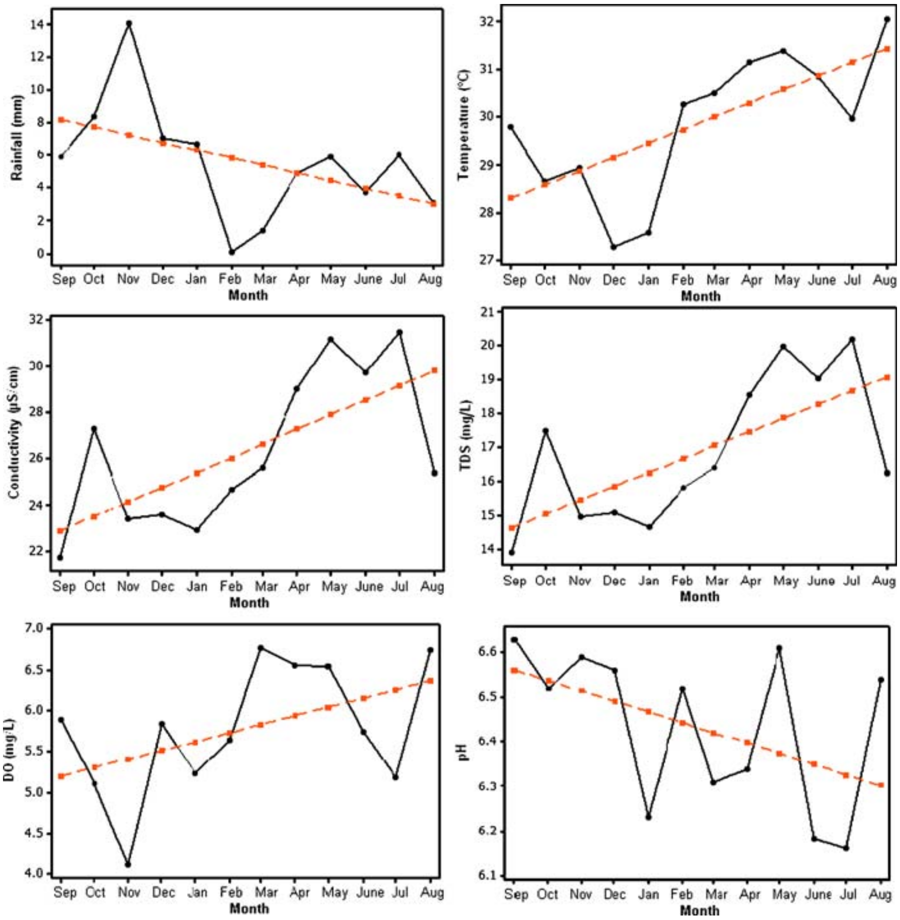

Fig. 2 Trends of rainfall and physical chemical parameters changes in water of Tasik Chini from September 2004 until August 2005

(MMS 2005). The month of November 2004 recorded the highest precipitation of 548.1mm and as the start of the raining season (Oct–Dec). This study shows that the mean (min–max) temperature, dissolve oxygen (DO), conductivity, pH, total dissolve solid (TDS) and water hardness of water in Tasik Chini for 12months sampling period at 15 sampling stations were 29.87°C (27.28–32.06°C), 5.78mg/l (4.11–6.77mg/l), 26.33µS/cm (18.94–31.50µS/cm), 6.43 (6.16–6.63), 16.85mg/l (13.90–20.17mg/l) and 7.54mg/l $CaCO_3$ (5.32–9.63mg/l) respectively. Results showed that there was an upward trend of chemical and physical variables changes such as temperature, conductivity, TDS and DO with different months (seasonal changes) and a downward trend for pH (Fig. 2). Spatial changes showed an upward trend of chemical and physical variables changes between sampling stations (Fig. 3). Statistical analysis shows that all parameters measured in this study (except for pH) have significant differences ($p < 0.05$) between the sampling months (ANOVA and Tukey–Kramer or Kruskal–Wallis and Mood's median test) and between sampling stations (except for temperature). High precipitation during the monsoon season resulted in low water temperature, conductivity, TDS, water hardness and to some extent DO. Stations 5 and 6 recorded lowest DO, temperature and to some extent pH value compare to other stations in the lake. This is due to the flowing incoming flood water from the Chini River where these sampling stations were most affected because it is located near the river mouth of Chini River (Fig. 1). Low DO is probably due to high suspended solid in the flood water where similar condition was reported in Tasek Bera during the great

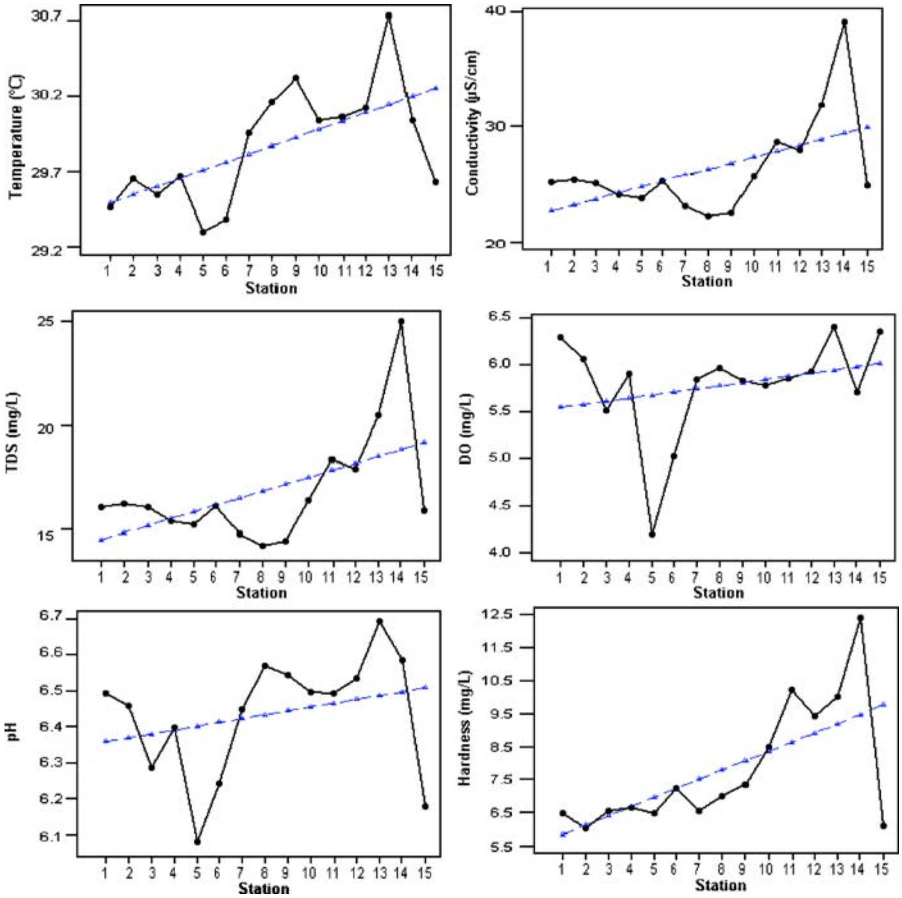

Fig. 3 Trends of physical chemical parameters changes in water of Tasik Chini at 15 samping stations for 12 months periods (—■— Actual, —■— Fit)

floods in raining season (Ikusima et al. 1982). Higher conductivity, water hardness and TDS reading were recorded at stations 11–14 as these stations were near to iron-mining areas which has been re-activated. Some effluents from the mining area were believed has been discharge into the lake and also through seepage. Detail on other water quality changes in Tasik Chini was discussed in Shuhaimi-Othman et al. (2007). In terms of water hardness, Tasik Chini water is classified as very soft water (i.e. <10mg/l) with very low calcium and magnesium ions. In comparison to other freshwater lake such as Tasek Bera, the largest natural lake in Peninsular Malaysia which is located about 50km from Tasik Chini showed a mean water hardness of 5.42mg/l (Ikusima et al. 1982) and also other Malaysian freshwaters (Johnson 1967; Shuhaimi-Othman et al. 2006). This 'poverty' especially in calcium is reflected by the scarcity of 'shell' animals in this lake (Abas et al. 2005) and also in Tasek Bera (Ikusima et al. 1982). Maimon and Farah (2005) reported that two main family of snails found in Tasik Chini were Viviparidae (98%) and Ampullariidae (2%). The paucity of calcium and magnesium in these lakes is similar to that of the lakes in the Amazon basin (Sioli 1968). In view of metal toxicity, it is well understood that decrease in water hardness can increase metal toxicity (Howarth and Sprague 1978; Stephenson 1983; Gill and Epple 1992) and this made Tasik Chini water and the organisms sensitive to metal pollution.

Results show that the mean (min–max) metal concentrations (in micrograms per liter) in Tasik Chini lake during the 12 months sampling at 15 sampling stations for Fe, Al, Mn, Ba, Zn, Pb, Cu and Cd were 794.84 (309.33–1,609.07), 194.53 (62.37–665.93), 29.16 (16.68–79.85), 22.07 (15.64–

29.71), 5.12 (2.224–6.553), 2.36 (1.165–4.240), 0.832 (0.362–1.443) and 0.421 (0.254–0.696) respectively. Generally, metal concentrations in the lake water was found in a decreasing sequence of Fe > Al > Mn > Ba > Zn > Pb > Cu > Cd. Statistical analysis shows that all metals measured in this study have significant differences ($p < 0.05$) between the sampling months (ANOVA and Tukey–Kramer or Kruskal–Wallis and Mood's median test) and between sampling stations (except for Zn, Pb, Cu and Cd). Concentration for three metals i.e. Ni, Cr and Co were too low and were not detected by the graphite furnace AAS. Comparison with various water quality standards showed that the mean Cu, Cd, Pb, Zn, Mn and Ba concentration in surface water of Tasik Chini were low and within the range of natural background concentration (Table 1). Although the mean of Fe concentrations was higher than the Canadian standard (CCME) it was found to be lower than United State Environment Protection Agency (USEPA (CMC)) and the Malaysian standard (INWQS). The mean value for Al concentration was higher than CCME and USEPA (CCC) standards (Table 1). These results are comparable with the study conducted in Tasek Bera, Pahang which showed that the mean (range) of Fe and Al was 0.64 (0.18–1.95) mg/l and 0.197 (0.045–0.37) mg/l respectively (Ikusima et al. 1982).

In general, metal concentrations in Tasik Chini lake water varies with season and the location of the sampling stations. Metal concentrations showed a seasonal fluctuations (Fig. 4) where the concentrations increased during the monsoon seasons, then declined at the end of the monsoon at the onset of the dry season. Studies carried by Shuhaimi-Othman et al. (2007) showed that during wet season (Oct–Dec), reverse flow of flooded water from Pahang River contributed to high suspended solids (as TSS and turbidity) to the Tasik Chini lake. This increased the influx of metals in Tasik Chini especially metals such as Fe, Al, Mn, Pb, Cu and Cd. Correlation analysis showed significant relationship between metal concentrations such as Fe and rainfall ($r = 0.493$, $p < 0.001$) and between Fe, Al, Cu and concentration of total suspended solid ($r = 0.408$, 0.579 and 0.544 respectively, $p < 0.001$; Table 2). Similar condition was reported in Tasek Bera lake with increase in calcium, magnesium, iron and aluminum concentrations in water in relation to season changes (Ikusima et al. 1982). Ikusima et al. (1982) suggests complex interaction phenomena particularly from the release of these minerals by decomposing organic matter during the dry season, and their influx in the monsoons from the watershed, together with their efflux from flood discharge and their use by organisms during population

Table 1 Criteria of metal concentrations in freshwater ecosystems

Metal	Present study (μg/l)	CCME-Protection of aquatic life (μg/l)	USEPA-Criteria maximum concentration (CMC) μg/l	USEPA-Criterion continuous concentration (CCC) μg/l	INWQS Class II (μg/l)
Copper (Cu)	0.832	2–4	13	9.0	20
Cadmium (Cd)	0.421	0.017	2.0	0.25	10
Lead (Pb)	2.36	1–7	65	2.5	50
Zinc (Zn)	5.12	30	120	120	5,000
Chromium[a] (Cr)	nd	8.9	570	74	50[b]
Nickel (Ni)	nd	25–150	470	52	50
Iron (Fe)	794.84	300	–	1,000	1,000
Manganese (Mn)	29.16	–	–	–	100
Aluminum (Al)	194.53	5–100	750	87	–
Barium (Ba)	22.07	–	–	–	1,000
Cobalt (Co)	nd	–	–	–	–

Sources: CCME 1999; INWQS (Tong and Goh 1997); USEPA 2005

nd Not detected by graphite furnace AAS

[a] Trivalent chromium (Cr(III))

[b] Hexavalent chromium (Cr(VI))

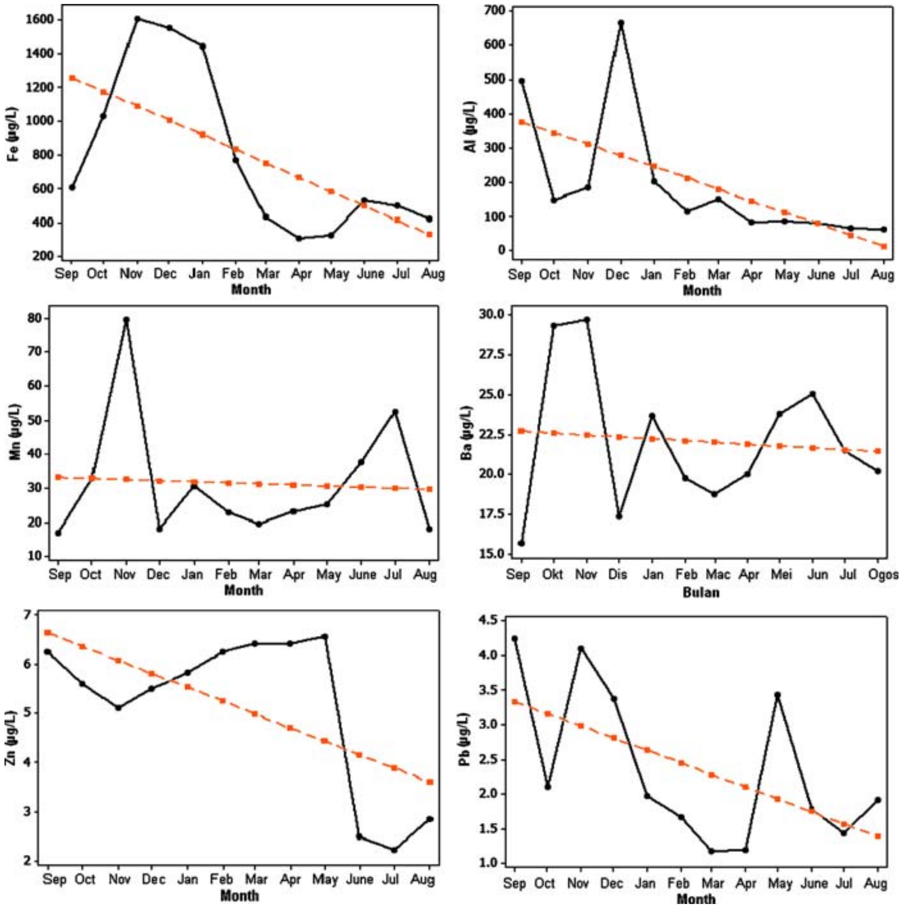

Fig. 4 Trends of metal changes in water of Tasik Chini from September 2004 until August 2005

growth. Heavy rain can also enhance the leaching of colloidal and precipitated iron from the soil and the leaf litter on the forest floor. The converse happens in the dry season when the mobility of iron and aluminium is reduced (Sioli 1968). However a study conducted in Tasek Bera showed that high iron value was dominant during the dry season (Feb–Apr) which was due to decomposition and resulted in partial or total anaerobic conditions where iron would be reduced to the soluble ferrous state (Ikusima et al. 1982).

The metal concentrations were found to vary with varies sampling station in the lake. At stations 5 and 6 high concentration of Fe and Al was found and to some extent Cu and Cd (Fig. 5). These stations which were located near to the Chini River were influenced by flooded water which is high in total suspended solid and metals (Fe and Al), flowing in from Pahang River via these stations. Stations 10 to 12 were found to have high concentration of Mn and Ba while station 13 with Mn. This incident can be related to the re-activation of the formerly closed iron-mine where current activities affected the nearby stations as shown by its high conductivity readings at these stations (Fig. 3). Sulphate concentration was also high at station 11 and 12 and also to some extent at station 10 (Shuhaimi-Othman et al. 2007). Correlation analysis shows significant relationship between sulphate and Ba concentration (r=0.318, p<0.001; Table 2). Mining waste from iron-mining area were believed to exists in the form of sulphate mineral especially barite ($BaSO_4$). Mn and Ba concentrations were also found high at these stations (stations 10 to 12) especially during raining season where some effluents from the mining area were believed to have been discharge into the lake and via groundwater seepage. Correlation analysis shows significant rela-

Table 2 Pearson correlation coefficient (*r*) between water quality parameters, metals and the rainfall

	Temp.	Cond.	TDS	DO	pH	Hard.	SO_4^{-}[a]	TSS[a]	Fe	Mn	Al	Ba	Cu	Cd	Pb	Zn
Cond.	0.127															
TDS	0.257***	0.961***														
DO	0.495***	0.028	0.103													
pH	0.130	0.074	0.119	0.308***												
Hard.	0.277***	0.573***	0.627***	0.120	0.246**											
SO_4^{-}[a]	0.139	0.334***	0.318***	0.126	0.136	0.260***										
TSS[a]	−0.475***	−0.047	−0.075	−0.103	0.191*	−0.147	−0.008									
Fe	−0.706***	−0.269***	−0.332***	−0.591***	−0.050	−0.334***	0.102	0.408***								
Mn	−0.160*	0.131	0.094	−0.437***	−0.061	−0.015	−0.073	−0.099	0.379***							
Al	−0.389***	−0.126	−0.162*	−0.243**	0.020	−0.132	−0.064	0.579***	0.391***	−0.068						
Ba	0.036	0.179*	0.175	−0.160*	0.108	0.295***	0.318***	−0.133	0.070	0.386***	−0.134					
Cu	−0.228***	0.108	0.062	−0.126	0.192*	0.003	0.252**	0.544***	0.212**	0.057	0.265***	0.050				
Cd	−0.252***	−0.009	−0.050	−0.197**	0.052	0.026	0.040	0.128	0.224**	0.060	0.102	−0.105	0.189*			
Pb	−0.140	−0.135	−0.160	−0.107	0.290***	−0.067	0.042	0.225**	0.260***	0.113	0.250**	−0.020	0.271***	0.177*		
Zn	−0.160	−0.022	−0.139	0.154	0.277***	−0.051	0.179*	0.089	0.022	−0.097	0.089	−0.038	0.149*	0.153*	0.094	
rainfall	−0.474***	−0.021	−0.085	−0.484***	0.149*	−0.054	0.065	0.106	0.493***	0.558***	0.114	0.205**	0.176*	0.254**	0.325***	0.006

*Significant relationship ($p<0.05$)

**Significant relationship ($p<0.01$)

***Significant relationship ($p<0.001$)

[a] TSS and sulphate (SO_4^{-}) data were from Shuhaimi-Othman et al. (2007)

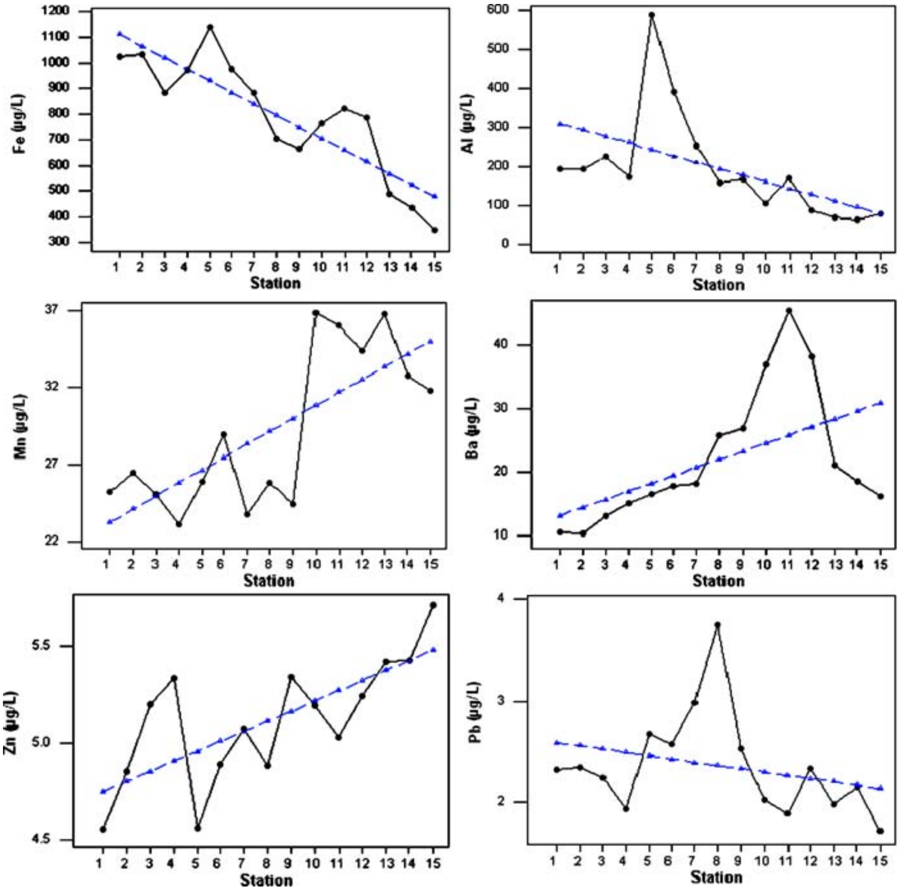

Fig. 5 Trend of metal changes in water of Tasik Chini at 15 samping stations for 12 months periods

tionship between rainfall and metal concentration of Mn (r=0.558, p<0.001) and Ba (r=0.205, p<0.01; Table 2).

Conclusions

The present study showed that metal concentrations in Tasik Chini water is still low and in the range of natural background concentration except for Fe and Al. Generally, metal concentrations of the water were found to decrease in the order of Fe>Al>Mn>Ba>Zn>Pb>Cu>Cd. Metal concentrations in the lake water varies with season and the location of the sampling stations. High precipitation during wet season can generate changes to the metal concentrations in the water through reverse flow of flood water from Pahang River resulting in high concentration of metals especially Fe and Al. The revival of abandoned mines had contributed to the increase in Ba and Mn concentrations in the lake water bodies. Stations located at the Tanjung Jerangking and Melai areas (St. 5, 6, 10, 11, 12 and 13) were the most effected area due to seasonal changes and human activities. It is proposed that mining activities should be stopped or minimized during the heavy raining season as the incoming flooded water into the lake already pose a high risk of metal influx into the lake. The authority in charge of the lake should consider monitoring plans to be incorporated in their resource management plans as the aquatic life which the community depends on may be at risk to biological loss.

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