The Relationship between Heavy Metals and Trophic Properties in Sembrong Lake, Johor
(Hubungan antara Logam Berat dan Sifat Trofik di Tasik Sembrong, Johor)

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ABSTRACT

The relationship between heavy metal and trophic properties in polymictic lake at Sembrong Lake, Peninsular Malaysia was assessed. Sixteen parameters, including heavy metals and trophic parameters were monitored. pH, temperature, dissolved oxygen and heavy metals level changes significantly influenced by the dynamic of polymictic mixing pattern. The mean concentrations of heavy metals in the reservoir decreased in the following order: Fe > Mn > Zn > Cu > As > Pb. The result showed that this polymictic lake is being threatened by cultural eutrophication with TSI value range from 72.40 to 80.41 and classified as a hypereutrophic lake. The levels of heavy metal pollution in the reservoir range from slightly polluted to polluted. Factor analysis was performed to determine the relationship between heavy metals and trophic parameters. Five factors were responsible for data structure and explained the 83% of total variance. These factors differentiate each group of parameters according to their common characteristics. Photosynthesis, respiration and redox processes were main factors contributing to the variability of both properties.

Keywords: Cultural eutrophication; factor analysis; heavy metal; hypereutrophic; photosynthesis; polymictic; redox process; respiration

ABSTRAK

Hubungan antara logam berat dan sifat trofik di tasik polimik di Tasik Sembrong, Semenanjung Malaysia telah dinilai. Enam belas parameter, termasuk logam berat dan parameter trofik telah dipantau. pH, suhu, oksigen terlarut dan tahap perubahan logam berat ketara dipengaruhi secara dinamik oleh corak pergaulan polimik. Min kepekatan logam berat dalam takungan menurun dalam susunan yang berikut: Fe> Mn> Zn> Cu> As> Pb. Hasil kajian menunjukkan bahawa tasik polimik ini sedang diancam oleh eutrofikasi budaya dengan TSI julat nilai 72.40-80.41 dan dikelaskan sebagai tasik hipereutrofik. Tahap pencemaran logam berat dalam pelbagai takungan daripada sedikit tercemar kepada tercemar. Analisis faktor telah dijalankan untuk menentukan hubungan antara logam berat dan parameter trofik. Lima faktor bertanggungjawab untuk struktur data dan menjelaskan 83% daripada jumlah varians. Faktor-faktor ini membezakan setiap kumpulan parameter mengikut ciri-ciri yang biasa mereka. Proses fotosintesis, pernafasan dan redoks merupakan faktor utama yang menyumbang kepada kepelbagaian kedua-dua sifat.

Kata kunci: Analisis faktor; eutrofikasi budaya; fotosintesis; hipereutrofik; logam berat; pernafasan; polimik; proses redoks

INTRODUCTION

The mixing pattern of water column can bring about dramatic changes in aquatic ecosystem. Therefore understanding the dynamic, physical, chemical and trophic status is crucial in order to determine the response of modification natural ecosystem to human-dominated ecosystem. Theoretically, mixing processes are mainly influenced by the geographical distribution and physical characteristic of water body and climate (Geller 1992). Dodson (2004) explained that lakes in tropical region are predominantly undergoing polymictic mixing process. Polymictic lakes lead to responsive lake ecosystem due to hot and humid weather changes throughout the year. Mixing pattern controls transport mechanism and biochemical processes in lake ecosystem such as evaporation, photosynthesis and respiration process (Degermendzhy et al. 2010; Halder et al. 2012; Koretsky et al. 2012; Lawson & Anderson 2007).

The equilibrium of ecosystem interactions is a vital key to sustain ecosystem health. However, in developed and developing countries, land developments had increased over time, therefore maintaining ecosystem health water of water resources is challenging. The deterioration of aquatic ecosystem health will lead to toxicity and harms the aquatic ecosystem (Edet & Offiong 2002). Human-dominated ecosystem encompasses a wide range of human activities such as agriculture, mining, urbanization and industrialization. Those activities disturb the natural ecosystem interaction responses. It creates a complex network of interactions throughout the fresh water ecosystem. As a result, abundance accumulation

of metals and nutrients consequently becomes cultural eutrophication (Ahmad & Shuhaimi-Othman 2010; Amin et al. 2009; Cai et al. 2012; Micó et al. 2006, Mil-Homens et al. 2006; Wei & Yang 2010).

Cultural eutrophication has become a serious threat to aquatic ecosystems (Lundberg 2013; MacLeod et al. 2011; Sharip et al. 2012; Xu et al. 2010). Eutrophication is characterised by the response of ecosystem to the addition of artificial or natural substances especially chemical nutrients in water body. A lot of previous studies confirmed that nutrient enrichment have caused cultural eutrophication (Azizur Rahman & Hasegawa 2012; Cheng & Chi 2003; Lawson & Anderson 2007; Levine et al. 2012; Sharip et al. 2012; Wang et al. 2013). Nutrient enrichment could be observed from the excessive growth of aquatic plants, especially water hyacinth (Sharip et al. 2012). High densities of submerged water hyacinth may absorb solar energy and increase surface water temperature (Peeters et al. 2013). These effects could contribute to temperature and density differences in lakes that can facilitate an evolution of mixing dynamic.

Despite being the main source of water resources in the area, no information is available on the study on trophic and heavy metals properties of the Sembrong Lake. The hypothesis of this study is that the polymictic mixing pattern influences the trophic and physicochemical properties in tropical lakes. The objective of this study wass to determine the vertical pattern of trophic and heavy metals properties. In addition, the study also evaluated the relationship of trophic parameters and heavy metals.

MATERIALS AND METHODS

STUDY AREA

Sembrong Reservoir is located in the southern part of Peninsular Malaysia, between latitudes 3° 26' 42" N to 3° 26' 42" N and longitudes 102° 54' 18" E to 102° 55' 54" E (Figure 1). This man-made reservoir was constructed in 1984 and originally designated for flood mitigation, but has been used for irrigation and water supply since 1997. The deepest point recorded during the survey was 7 m, with a mean of 3.2 m. The lake floor has an average slope of 4%. The deepest part is located in the southern area near the spillway, with depths ranging from 5 to 7 m. The study area has a humid tropical climate. The mean annual temperature is 30°C, with a range of 25 to 38°C. The area receives a mean annual rainfall of 1913 mm. Based on a long-term rainfall data at Sembrong Station, heavy rainfall is frequently recorded during the northeast monsoon season from November to January (Figure 2). The southwest monsoon season between May and September brings less rainfall, with a recorded total monthly rainfall as low as 4.8 mm.
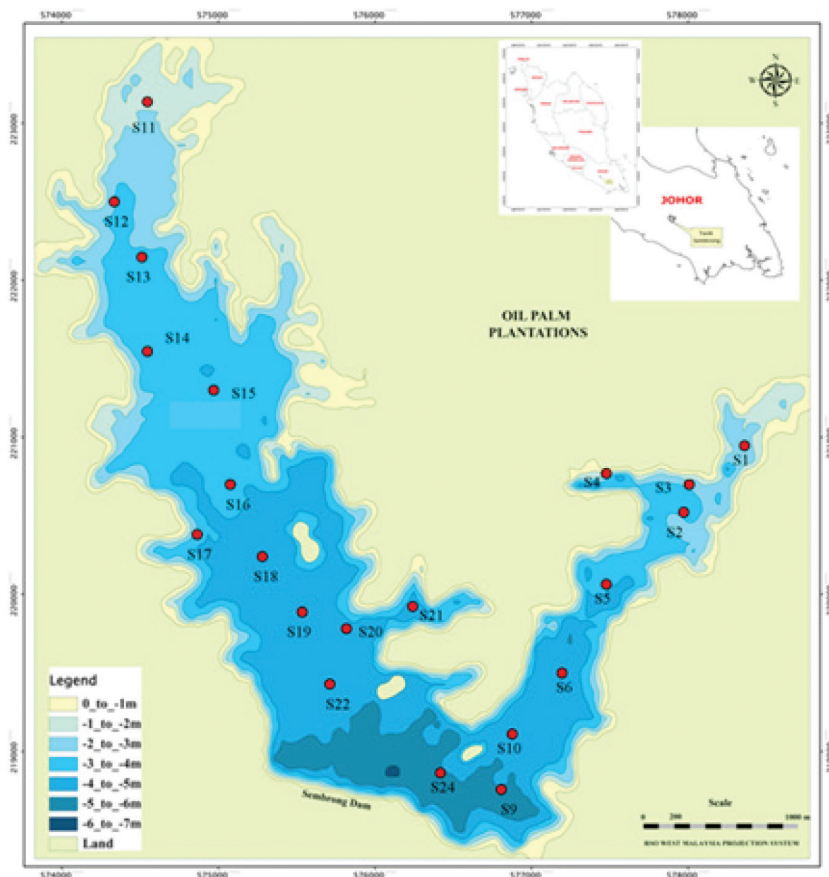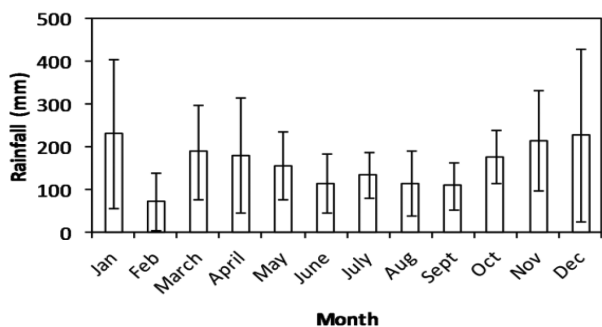

FIGURE 1. Bathymetric map of Sembrong Reservoir

*Note: Lines indicate standard deviation

FIGURE 2. Mean monthly rainfalls at Sembrong
Reservoir (2001 to 2011)

SAMPLE COLLECTION AND ANALYSIS

In order to evaluate the dynamics of the aquatic ecosystem, depth factor become an important factor (Huo et al. 2014). Therefore, vertical sampling program was conducted to evaluate the dynamics of the aquatic ecosystem. Vertical sampling programs were conducted on 23 November 2011, 15 February 2012 and 9 January 2013. The extensive spatial sampling programs were carried out on 16 February 2012 and 21 June 2012 to obtain 23 and 18 samples, respectively. The levels of total dissolved solid (TDS), electrical conductivity (EC), dissolved oxygen (DO), pH value, CA, salinity and temperature were measured *in situ* using a YSI 6600 multiprobe sonde. Water transparency was also measured using a Secchi disk.

Water samples were collected for the laboratory analysis using horizontal Van Dorn sampler. Two samples were collected at each point for nutrient and heavy metal analyses. All sampling procedures, storage, pretreatment requirements and analytical methods followed the standard method of the United States Environmental Protection Agency (Ahmad et al. 2009; Eaton & Franson 2005). The TP content was measured using a DR/2800 spectrophotometer. The elements Fe, Mg, Pb, Cu, Cd, Mn, Zn, and Al were measured using Perkin Elmer inductively coupled plasma optical emission spectrometers (Optima 5300 DV).

WATER QUALITY EVALUATION INDICES

Trophic Status   The TSI is widely used to assess the trophic status of the lake (Yen et al. 2012; Devi Prasad 2012; Liu et al. 2010). The tropic parameters of CA, SD and TP were used to calculate TSI.

$$\text{TSI (TP, µgL}^{-1}) = 10 \times \left[6 - \frac{\ln\left(\frac{48}{TP}\right)}{\ln 2} \right]. \tag{1}$$

$$\text{TSI (SD, m)} = 10 \times \left[6 - \frac{\ln(SD)}{\ln 2} \right]. \tag{2}$$

$$\text{TSI (CHL, µgL}^{-1}) = 10 \times \left[6 - \frac{2.04 - 0.68 \times \ln(CHL)}{\ln 2} \right]. \tag{3}$$

$$\text{TSI} = \text{TSI (TP)} + \text{TSI (SD)} + \text{TSI (CHL)} / 3. \tag{4}$$

Heavy metal pollution index   HEI determines the overall water quality with respect to level of heavy metals and is expressed as

$$\text{HEI} = \Sigma_{i=1}^{n} \frac{H_c}{H_{mac}}, \tag{5}$$

where H_c is the measured value; and H_{mac} is the maximum admissible concentration (MAC) of the i_{th} parameter. HEI levels were classified as slight (HEI < 10), medium (10 > HEI < 20), or high (HEI > 20).

RESULTS AND DISCUSSION

SPATIAL DISTRIBUTION OF PHYSICOCHEMICAL PROPERTIES IN SEMBRONG LAKE

The summary of water quality parameters are given in Table 1. The pH values vary from 6.91 to 9.17, with an average of 7.69. These values were characterized from neutral to alkaline. Although the variance of pH is slight, the spatial distribution suggests that pH is generally neutral (6.5 > pH < 7.8) near the reservoir inlets (Sembrong River and Marpo River) and becomes alkaline (> 9) southward near the spillway (Figure 3). These findings suggested that water input may carry solutes from oil palm plantations and modern agriculture areas. These solutes were distributed into Sembrong Reservoir and thus decrease the pH values. These results were supported by the fact that the total dissolved solid TDS values were increasing at the inlets at a range of 65 to 121.8 mg/L (Figure 4). The level of EC varies from 99 to 190.3 µS.

This result indicated that the heavy metal concentrations in descending order were: Fe > Mn > Zn > Cu > As > Pb. Although the natural concentrations of heavy metals were difficult to distinguish because of the geochemical process in the reservoir, the high heavy metal concentrations obtained were indicative of additional sources. The results showed high concentrations of Fe and Mn, with means of 744.49 and 52.26 ug/L. The results also indicate that 100% of the samples showed Fe concentrations beyond the MAC value (200 ug/L). The Mn concentrations showed that 46% of the samples also exceed the MAC value (50 ug/L). The Pb concentrations in 34% of the samples are also higher than the MAC limit of 1.5 ug/L. However, the Cu, Zn and As concentrations were below their usual MAC values. These findings indicate that sources of Fe, Mn and Pb could be derived from the anthropogenic sources particularly from catchment area.

VERTICAL DISTRIBUTION OF PHYSICOCHEMICAL PROPERTIES IN SEMBRONG LAKE

Located in the tropical region, Sembrong lake experienced hot and humid weather all year round. With this hot weather and coupled with strong winds in the afternoon, could enhance the mixing process. Polymictic mixing often experience frequently bouts of mixing pattern (Dodson

TABLE 1. Summary of physicochemical water quality of Sembrong Reservoir

| Parameter	Mean	Min-Max	MAC	% > MAC
TDS	71.8	65-121.8		
EC (μS)	113.18	99-190.3	1400	
pH	8	6.91-9.17	6.5-8.5	
Mn (μg/L)	52.26	15.10-134.84	50.00	46
Cu (μg/L)	6.47	0-33	1,000.00	
Zn (μg/L)	46.25	3-270	5000	
Fe (μg/L)	744.49	370.56-3756.94	200	100
As (μg/L)	6.21	0.63-17.15	50	
Pb (μg/L)	3.05	0.002-11	1.5	34
Temperature	30.16	28.62-31.62		
Salinity	0.05	0.04-0.09		
TP	420	280-640		
Turbidity	6.72	0.00-18.6		
Chlorophyll (μg/L)	12.60	3.3-20.7		
Total phosphate	430.33	280-640		
Secchi depth (cm)	37	26-48		
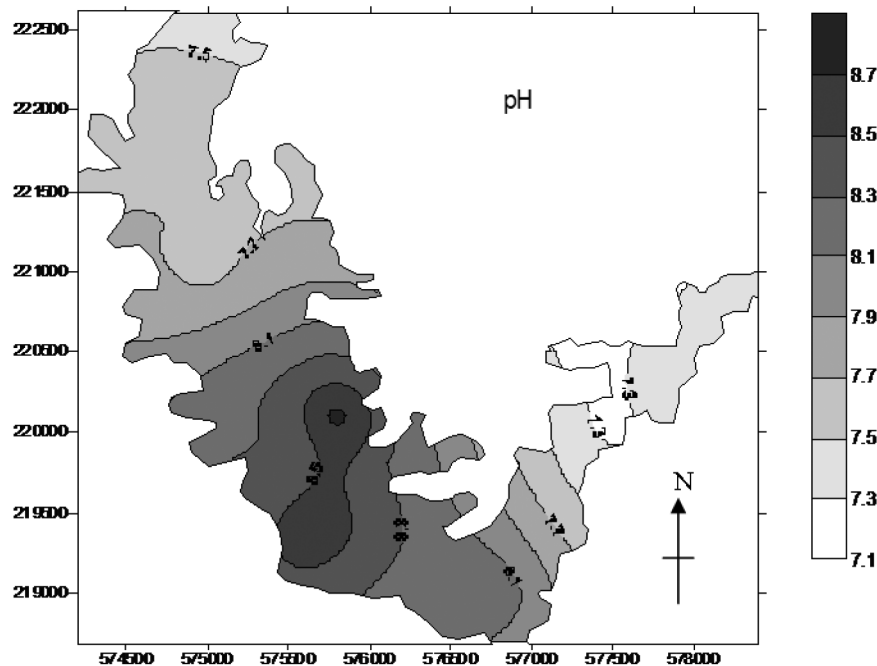
FIGURE 3. Distribution of pH value in Sembrong Reservoir

2004). The temperature profiles were relatively constant at depths between 0 and 2 m and slightly decrease at depths between 3 and 4 m (Figure 5). As expected in polymictic lake, the pH values also decreased with depth as a result of thermal stratification with depth at a gradient of 1°C. Near surface water was moderately alkaline but became acidic at the bottom. Vertical profiles on November, 2011 showed the increment of conductivity at 4 to 5 m depth corresponds to the high density at the bottom lake.

Vertical profiles of conductivity only showed a small depletion from surface water towards the bottom. The stratification pattern appeared to be obvious on wet months (November 2011). It also noted that the water level during

wet month increased and lake is deeper. Therefore, thermal stratification is more obvious in comparison to the dry months. During dry month, density stratification is less developed and creating bout mixing in lake system.

The surface layer (epilimnion) was saturated with DO with a mean of 8.71 mg/L, but only small changes of saturation level in which decreased gradually towards the bottom layer (hypolimnion) with a mean of 7.07 mg/L. The oxygen demand in this lake system mainly control by photosynthesis and respiration process. The result showed that mean values of chlorophyll and secchi depth were 12 ug/L and 37 cm, respectively. Both parameters become a proxy for abundant phytoplankton in this lake
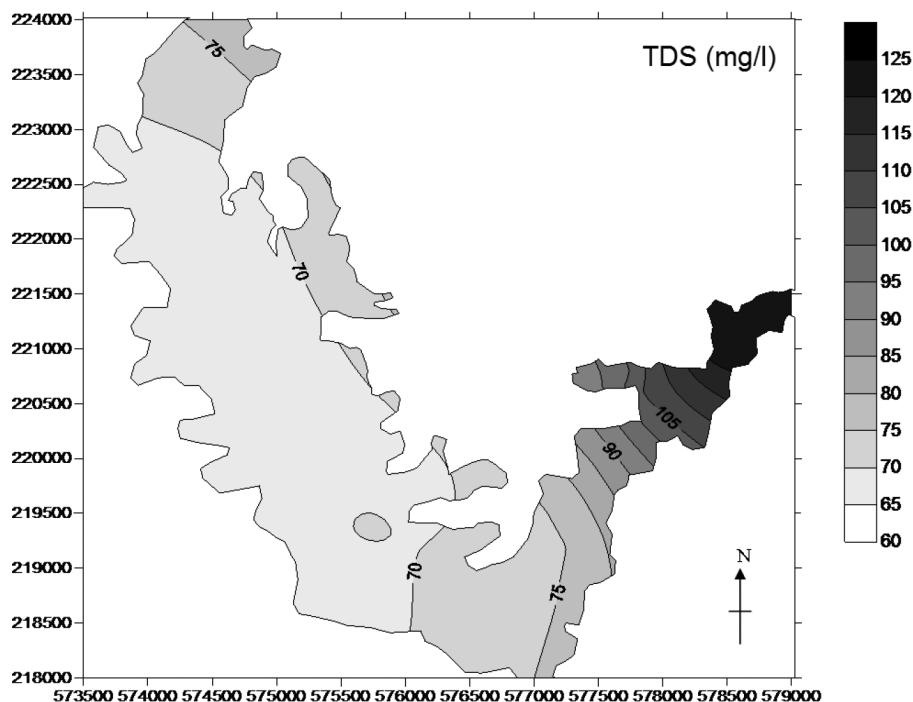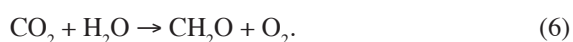
FIGURE 4. Spatial distribution of TDS value in Sembrong Reservoir

system. In the epilimnion layer, oxygen is released during photosynthesis (Bakar et al. 2014; Bellanger et al. 2004; Koretsky et al. 2012; Martins et al. 2008; Townsend 2002) in the following manner:

$$CO_2 + H_2O \rightarrow CH_2O + O_2. \tag{6}$$

As sunlight is limited at lower depths, photosynthesis becomes less significant compared with the respiration process by organisms and plants. O_2 is also needed in the decomposition of dead biomass at the bottom lake. Consequently, CO_2 increases and O_2 concentration decreased, thereby caused depleted oxygen toward the bottom layer. In an aqueous solution, CO_2 reacts with water molecules to produce carbonic acid, which subsequently dissociates into hydrogen and bicarbonate ions, as described in (7) (Gomes & Asaeda 2013; Koretsky et al. 2012). In this study, the excess H^+ resulted in the decrease of pH in the bottom layer and the decrease in DO with depth (Figure 6).

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-. \tag{7}$$
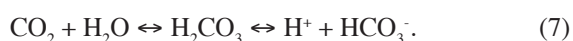
Electron activities increase and trigger the potential redox (reduction) reaction in deep layers. In a neutral environment with approximately pH7, Fe (III) and Mn (IV) form insoluble compounds and become terminal electron acceptors (Dodson 2004; Lovley 1991; MacLeod et al. 2011). Therefore, in the hypolimnion layer, Fe (III) is reduced to Fe (II), which also released the hydrogen ions and contributes to acidity. Fe (III) reduction can be described by the following reaction (Lovley 1991):

$$H_2 + 2Fe (III) \rightarrow 2H^+ + 2Fe (II). \tag{8}$$

At the present site, redox stratification at shallow depths (approximately 3 m) increased Fe (II) concentration from 2 to 6 mg/L and the acidity from a pH level of 7 to 6. An accumulation of reduced solutes or ions under hypolimnetic anoxia has been reported in other lakes at Kalamazoo and Barry Counties, Michigan, USA (MacLeod et al. 2011).

AQUATIC ECOSYSTEM STATUS

The degree of lake eutrophication is indicated by the TSI range from 72.40 to 80.41 (Table 2). Based on the TSI results, the Sembrong reservoir falls under the hypereutrophic state. The means of TSI were 63.43 for Chl, 74.81 for SD and 87.81 for TP. The value of the TSI for TP was generally higher than that for CA, which suggested that TP is a limiting factor for algal production in the reservoir.

The HEI results were presented in Table 3. The HEI values range from 2.77 to 19.53, with a mean of 5.86. Based on HEI, 95% of the samples were slightly polluted and the remaining 5% were polluted. Most of the more polluted samples were registered near the inlets, which are proximate to agricultural areas, whereas lower pollution concentrations were observed in the southern parts, especially near the spillway (Figure 7).

THE RELATIONSHIP BETWEEN PHYSICOCHEMICAL AND BIOMASS PARAMETER

Factor analysis was applied to gain reliable information on the relationship among parameters. The summary of
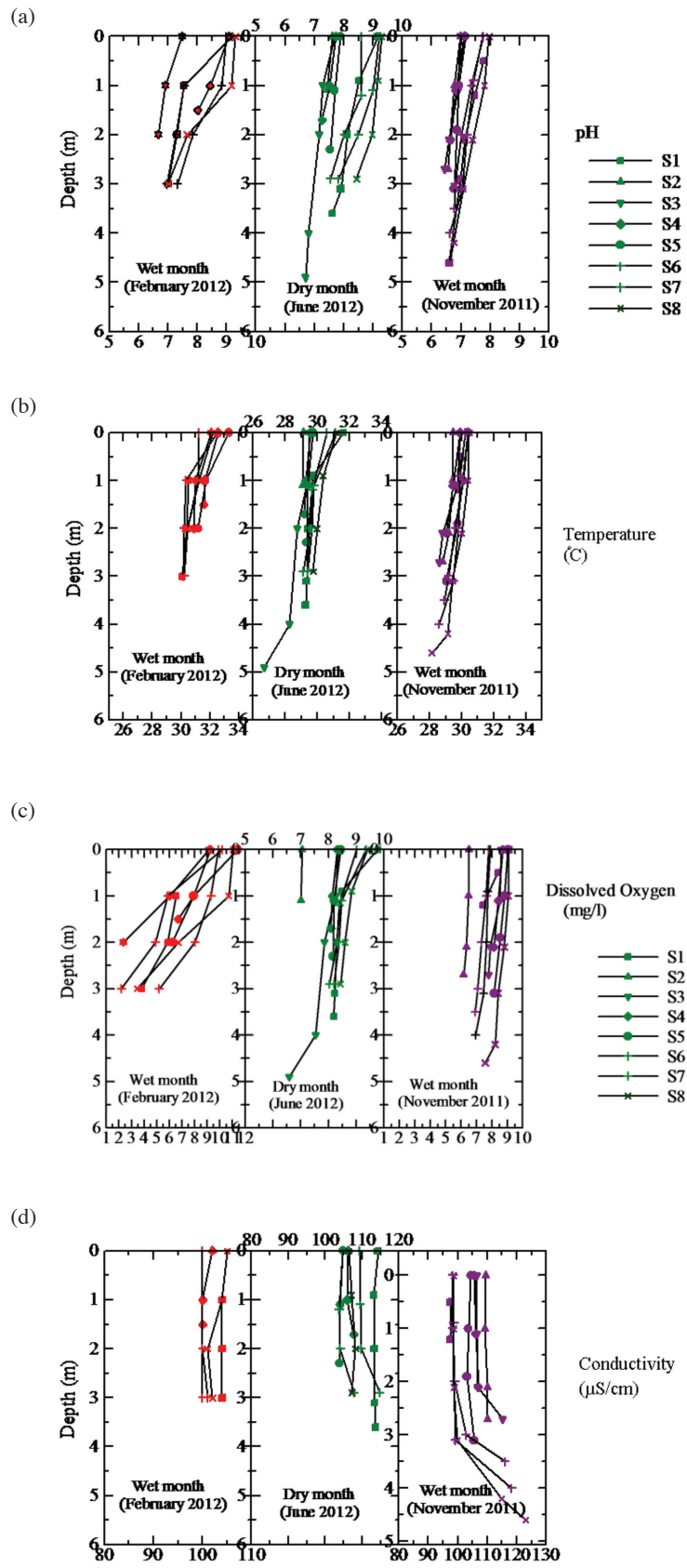
FIGURE 5. Profiles pattern of physical parameters a) pH, b) Temperature (°C), c) Dissolved Oxygen (mg/L) and d) Conductivity (μS/cm)
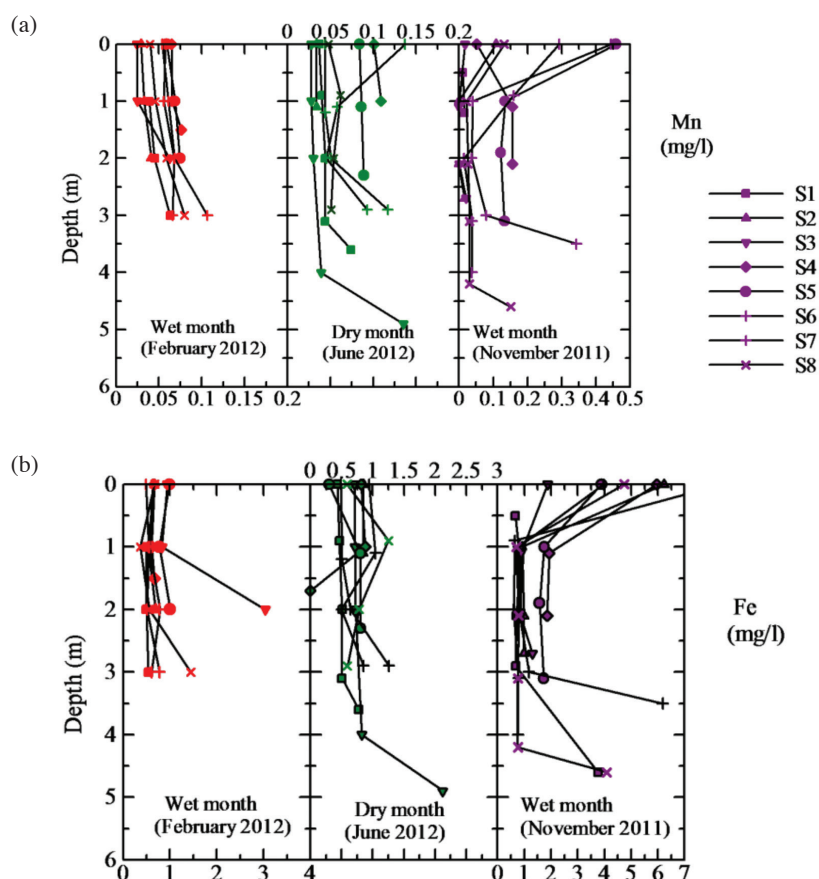
FIGURE 6. Profiles pattern of heavy metal concentrations (mg/L) a) Fe and b) Mn

TABLE 2. Summary of TSI values of Sembrong Reservoir

Trophic index	Min	Max	Mean
TSI (CHL)	59.63	65.97	63.73
TSI (SD)	70.59	79.43	74.84
TS (TP, µg/L)	85.44	97.37	92.28
TSI	72.4	80.41	76. 55

TABLE 3. Evaluation of heavy metal status in Sembrong Lake based on HEI criteria

Index method	Class	Description	Percentage
HEI	< 10	Slightly polluted	90%
	10–20	Medium polluted	10%
	>20	Highly polluted	-

the varimax component of water samples is illustrated in Table 4. Five significant components with eigenvalues higher than one were obtained.

Factor 1 accounts for 34% of the total variance and is characterized by positive loading on salinity, TDS and EC but negative loading on Mn. Salinity, TDS and EC were associated with one another because these parameters are related to the dissolved ion (solutes) content in the water body. The concentrations of TDS were higher near the inlets most likely because of modern agricultural sites. Crop cultivation results in an increased land opening and causes intense surface erosion, which subsequently transports more solutes into the reservoir (Gharibreza et al. 2013).

Factor 2 exhibits 21% of the total variance, with positive loadings on Cu, Zn and Pb. This factor indicates a strong association among parameters with r values ranging from 0.755 to 0.924. The mean concentrations of heavy metals were 6.47 (Cu), 46.25 (Zn) and 3.05 µg/L (Pb). The concentrations of Cu and Zn were below the MAC values at 1000 and 5000 µg/L, respectively,
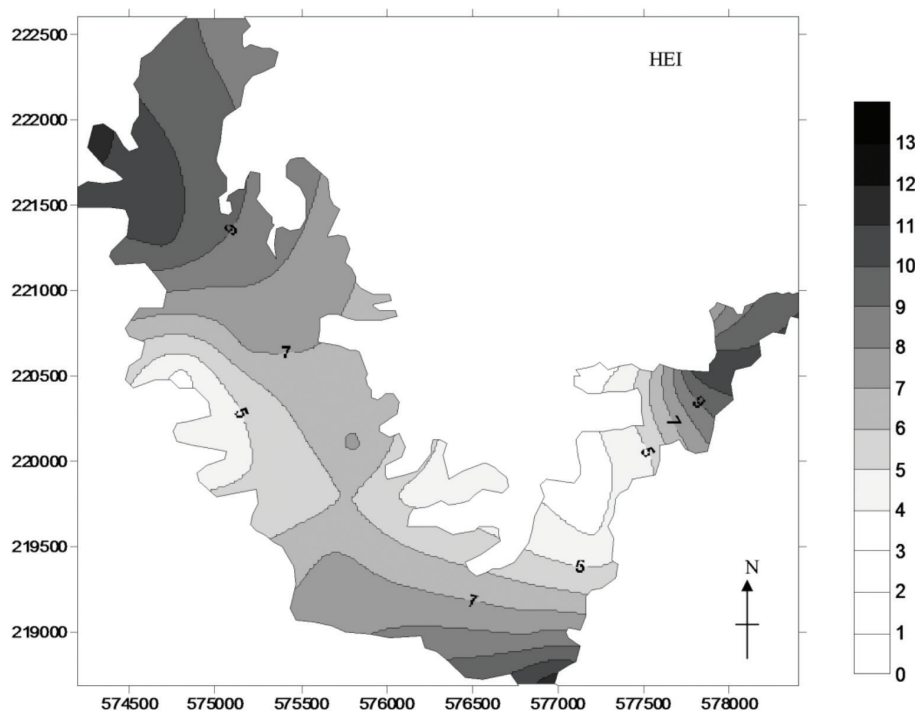
FIGURE 7. Spatial distribution of HEI values in Sembrong Reservoir

TABLE 4. Factor analysis of Sembrong Reservoir

Component	Eigen	Percentage of variance	Cumulative %	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Sal	5.068	33.787	33.787	**0.904**	0.094	0.046	0.154	0.149
TDS	3.250	21.664	55.451	**0.903**	0.197	-0.094	-0.194	0.264
EC	1.595	10.633	66.084	**0.902**	0.162	-0.099	-0.128	0.281
Mn	1.469	9.795	75.879	**-0.687**	0.295	-0.176	0.020	0.489
Cu	1.100	7.333	83.212	0.149	**0.924**	-0.215	-0.089	0.089
Zn	0.765	5.102		0.268	**0.922**	-0.098	-0.079	0.080
Pb	0.637	4.248		-0.244	**0.755**	-0.186	-0.436	0.155
SD	0.442	2.945		0.013	-0.184	**0.919**	0.289	0.039
DO	0.251	1.675		-0.045	-0.093	**0.847**	-0.193	-0.163
TP	0.174	1.162		0.022	-0.187	**0.773**	0.426	0.025
Chlorophyll *a*	0.095	0.630		-0.035	-0.340	0.233	**0.790**	-0.110
Temperature	0.067	0.447		-0.204	-0.349	-0.032	**0.762**	-0.355
As	0.051	0.340		0.016	0.061	0.086	**0.655**	0.179
Fe	0.028	0.188		0.150	0.159	-0.201	-0.180	**0.774**
pH	0.007	0.050		-0.352	-0.018	-0.132	-0.162	**-0.703**

Extraction method: Principal component analysis

which indicates that Cu, Zn and Pb were released from natural sources, especially from metamorphic sediments (Layang-layang formation) that contain chalcophylic metals (Loska & Wiechuła 2003). Although Pb can be derived from chalcophylic sources, the high value of Pb may suggest additional contributions from the application of pesticides and inorganic fertilizers, as well as atmospheric deposition (Bhuiyan et al. 2010; Prasanna et al. 2012).

Factor 3 accounts for 11% of the total variance, with positive loadings on SD, DO and TP. As expected, the algal

biomass related parameters, which were TP and SD became the main factors affecting water quality in Sembrong Reservoir, with values ranging from 280 to 640 µg/L and 26 to 48 cm, respectively. Based on the TSI values, the hypereutrophicity of the reservoir is a nutrient-limiting factor. Therefore, SD, DO and TP were associated with one another as a result of the hypereutrophic phenomenon.

Factor 4 accounted for 9.8% of the total variance and is characterized by positive loadings on CA, temperature and As. CA and temperature were related to each other because both serve major functions in the photosynthesis

process. CA is abundant in photosynthetic organisms, such as aquatic macrophytes. Water hyacinth was observed to grow rapidly in the Sembrong Reservoir, which may suggest eutrophication. Although As might originate from anthropogenic sources, the positive loadings among CA, temperature and As prove the capability of water hyacinths as a hyperaccumulator. Therefore, As attaches to water hyacinths. Previous studies explained that water hyacinths aid in the removal of heavy metals, such as As and Cu (Alvarado et al. 2008; Mishra & Tripathi 2009; Singh & Kalamdhad 2012; Zheng et al. 2009).

Factor 5 accounted for 8% of the total variance, with negative loadings on Fe and pH. Fe concentrations were high in almost all samples, with concentrations ranging from 370.56 to 3,756.94 µg/L. The high concentration of Fe suggested the presence of additional sources from anthropogenic activities, in addition to rock weathering. Moreover, the negative loading on pH indicates that Fe acts as Fe-oxyhydroxide and releases hydrogen ions as a result of the redox reaction of Fe (III) to Fe (II). Therefore, pH will decrease as Fe concentration increased.

Conclusion

In summary, this study showed that Sembrong Lake has been eutrophic and become hypereutrophic. Vertical profile sampling method improved understanding of aquatic ecosystem dynamic. The mixing pattern is a key factor controlling the physical and chemical processes in aquatic ecosystem. Aquatic ecosystem status indicated that this polymictic lake undergoing hypereutrophic. HEI suggested that 95% of the samples were only slightly polluted.

This study found that the relationships between natural and anthropogenic sources were highly correlated in controlling aquatic ecosystem status. Aquatic ecosystem status in Sembrong lake poses a threat to ecological habitats. Further studies, especially on nonpoint source pollution, were required to establish the influence of long-term human activities in order to sustain aquatic ecosystem.

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