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Heavy metal concentrations in water and sediments in Tasik Chini, a freshwater lake, Malaysia

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Abstract The purpose of this paper are to determine the concentration of heavy metals namely cadmium (Cd), copper (Cu) and lead (Pb) in water and sediment; and to investigate the effect of sediment pH and sediment organic matter on concentration of cadmium, copper and lead in sediment at oxidation fraction. For this purpose the concentration of heavy metals were measured in water and sediments at 15 sites from Tasik Chini, Peninsular Malaysia. The sequential extraction procedure used in this study was based on defined fractions: exchangeable, acid reduction, oxidation, and residual. The concentration of heavy metals in residual fraction was higher than the other fractions. Among the non-residual fractions, the concentration of heavy metals in organic matter fraction was much higher than other fractions collected from all sampling sites. The pH of the sediment in all sites was acidic. The mean pH ranges from 4.8 to 5.5 with the higher value observed at site 15. Results of organic matter analysis showed that the percentage of organic matter present in sediment samples varies throughout the lake and all sites of sediments were relatively rich in organic matter ranging from 13.0% to 34.2%. The highest mean percentage of organic matter was measured at sampling site 15, with value of 31.78%.

Keywords Concentration · Heavy metals · Individual contamination factor · Sediments · Sequential extraction · Tasik Chini

Introduction

Heavy metal concentrations in aquatic ecosystems are usually monitored by measuring its concentration in water, sediments and biota (Camusso et al. 1995) which generally exist in low levels in water and attain considerable concentration in sediments and biota (Namminga and Wilhm 1976). Heavy metals including both essential and non-essential elements have a particular significance in ecotoxicology, since they are highly persistent and all have the potential to be toxic to living organisms (Storelli et al. 2005).

Heavy metals do not exist in soluble forms for a long time in waters; they are present mainly as suspended colloids or are fixed by organic and mineral substances (Kabata-Pendias and Pendias 2001). In aquatic ecosystems, water contamination by heavy metals is one of the main types of pollution that may stress the biotic community (Baldantoni et al. 2004).

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Sediments are important sinks for various pollutants such as heavy metals (Eimers et al. 2001; Clements and Newman 2002; Ho et al. 2003; Ikem et al. 2003) and also play a useful role in the assessment of heavy metal contamination (Gangaiya et al. 2001). The release of heavy metals from sediments into the water body and consequently to biota will depend on the speciation of metals and other factors such as sediment pH and organic matter. Heavy metals may distribute in sediments as exchangeable bound, iron–manganese oxide bound, organic matter bound and residual bound species (Dean 2002). They generally exhibit different physical and chemical behavior in terms of chemical interactions, mobility, biological availability and potential toxicity (Xiangdong et al. 2000). Measurement of total metal concentrations in sediment is useful to detect any net change, but does not give any indication about the chemical form of metals in sediment (Otero et al. 2000; Pagnanelli et al. 2004).

In this study, sequential extraction method was used to determine the distribution and concentration of cadmium, copper and lead in sediments. The distribution and concentration of these metals in water was also measured. For this purpose, the samples of water and sediment were collected and analyzed based on the selected sites. The objectives of this study were to determine the distribution and concentration of three heavy metals, i.e., cadmium (Cd), copper (Cu) and lead (Pb) in water and sediments and to investigate the effect of sediment pH and sediment organic matter on concentration of cadmium, copper and lead in Tasik Chini, a freshwater lake.

Material and methods

Study area

Tasik Chini as it is locally called or Lake Chini is one of the two natural lakes in Malaysia. It is located in east of Peninsular Malaysia. Its latitude and longitude coordinates are from 3° 24′ 40″ to 3° 26′ 42″ N and 102° 54′ 18″ to 102° 55′ 54″ E respectively. The lake covers an average area of about 200–400 ha depending on the season, comprising of 12 adjoining water bodies giving it the characteristic finger-like projections. It has a humid tropical climate and annual rainfall is from 1,488 to 3,071 mm (Islam et al. 2005). Apart from its significance as multitude uses including boating, outdoor recreational activities, commercial and recreational fisheries, Tasik Chini is an area of ecological importance due to its great biodiversity and it is also of considerable importance for the local economy. During recent years, the land area around lake has been developed for ecotourism and agriculture. At sampling sites 8 and 9, there are plantations and in around sites 14 and 15 there are numerous abandoned metal mines. Near site 3, there are several boat stations. These activities could be the source for pollution to the lake.

Water and sediments sampling

Water and sediment samples were collected 4 times (from October 2004 to July 2005) for every 3 months from 15 sites in the lake (Fig. 1). Water samples were collected into acid washed 250-ml plastic bottles from approximately 30 cm below the surface water. Sediment samples were collected using grab sampler from 15 sites. Prior to any analysis, all equipment and containers were soaked in 10% HNO3 and rinsed thoroughly with deionized distilled water before use.

Water and sediments analysis

The water samples were filtered using a 0.45 μm nitrocellulose membrane filter. Samples of sediments were oven dried, sieved through a 63 μm mesh and weight to 10 g. The pH of the sediments was measured in distilled water with a 1: 2.5 sediment/solution ratio (Madejon et al. 2002; Guevara-Riba et al. 2004). The content of organic matter in each sample was determined using loss on ignition. Portions of 5.0 g oven dried sediment from each site were heated at 450°C (Manta et al. 2002; Andrews and Sutherland 2004; Guevara-Riba et al. 2004) for 20 h. Each sample was re-weighted after being cooled to determine level of organic content by the loss in weight of dry sediment.

In this study, sequential extraction procedure was used and conducted with modification by adopting the method of Badri and Aston (1983). This procedure consists of four stages. The extraction steps employed in this study are described as follows: Extraction 1 – *Easily and Freely Leachable and Exchangeable fraction*: 50 ml 1 M NH_4CH_3COOH at

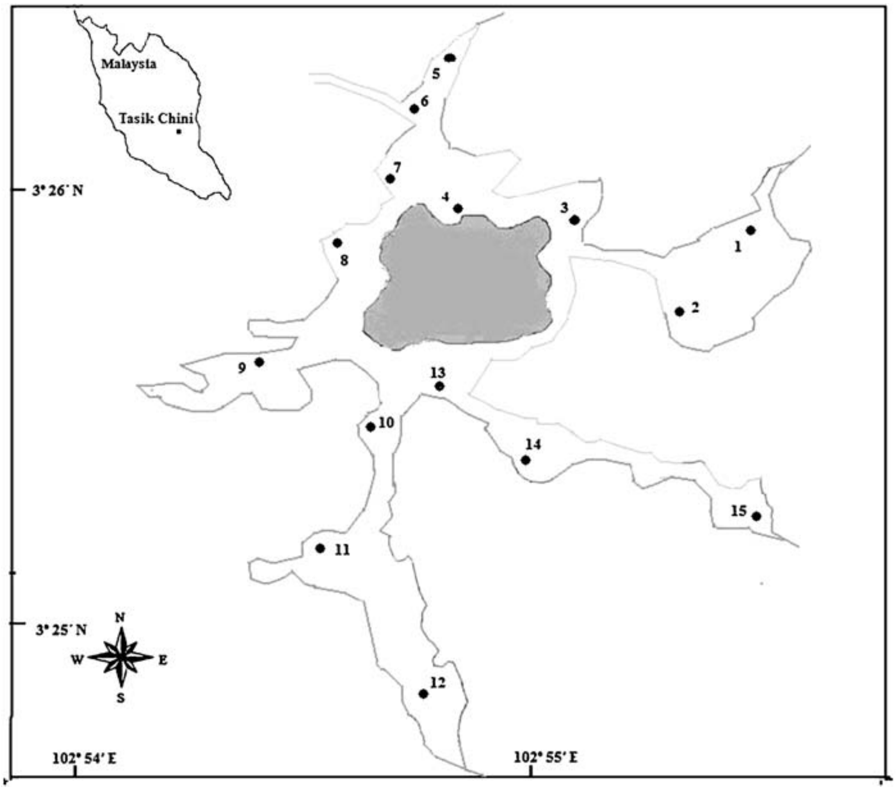

Fig. 1 Map of the sampling sites in Tasik Chini

pH 7 was added to the weighted sample into bottle and the sample was shaken for 90 min at a speed of 15 rpm at room temperature. Extraction 2 – *Acid Reduction Fraction*: 50 ml 0.25 M $CH_2OH{\cdot}HCl$ at pH 2 (adjusted using HNO_3) was added to the residue from Fraction 1, and the sample was shaken under the same settings described in Fraction 1. Extraction 3 – *Organic Oxidation Fraction:* 15 ml H_2O_2 30% was added to the residue from Fraction 2 and the sample was placed in water bath until dry. Then, 50 ml 1 M NH_4CH_3COOH at pH 3.5 (adjusted using HCl) was added to it, and the sample was shaken under the same settings described in Fraction 1. Extraction 4 – *Resistance Fraction:* Residue from Fraction 3 was used for final fraction. The sample was placed in a PTFE beaker and added 5:2 $HNO_3/HClO_4$ ratios (*v*/*v*). The sample was placed on a hot plate and heated until the solution became clear. At the end of each fraction the samples were centrifuged for 30 min at 1,500 rpm to separate the sediment. The sediment was washed in 50 ml of deionized distilled water and again centrifuged. The washed water was discarded. Before analysis, the samples were filtered using a 0.45-μm nitrocellulose membrane filter. The determination of cadmium, copper and lead in water were carried out by graphite furnace atomic absorption spectrometer (Perkin Elmer, Analyst 800), and in sediment by flame atomic absorption spectrometer (Perkin Elmer 1100B). All samples were analyzed in three replicates.

Statistical analyses

Pearson's correlation coefficients (*r*) were used when calculating correlations between pH, organic matter and concentration of heavy metals at oxidation fraction. To determine the significant differences at different sampling sites of the four sediment fractions, a one-way analysis of variance (ANOVA), Tukey's honest significant difference test was employed. This is because of normalization of data. The Kruskal–Wallis test used to determine the significant differences at different sampling sites in water because of homogeneity of variances. Data were tested for normality (Anderson–Darling's test) and homogeneity (Levene's test). Data analyses were carried out using the statistical package Minitab (Release 14).

Results

Heavy metal concentration in water

Concentrations of cadmium, copper and lead in water from each sampling site are given in Table 1. The highest mean concentration of cadmium in water was measured at site 9 at 0.32 μg l^{-1}, with values ranging from 0.04 to 1.04 μg l^{-1} while the lowest mean concentration of it in water was measured at site13 at 0.06 μg l^{-1}, with values ranging from 0.01 to 0.10 μg l^{-1}. The highest mean concentration of copper in water was measured at site 2 at 8.36 μg l^{-1}, with values ranging from 1.10 to 26.36 μg l^{-1} while the lowest mean concentration of copper was measured at site 14 at 1.50 μg l^{-1}, with values ranging from 0.65 to 2.60 μg l^{-1}. The highest mean concentration of lead in water was measured at site 3 at 18.7 μg l^{-1}, with its ranged values from 1.70 to 57 μg l^{-1} while the lowest mean concentration of lead in water was measured at site12 at 2.85 μg l^{-1}, with values ranging from 1.72 to 4.96 μg l^{-1}.

pH and organic matter in sediments

The values of pH and percentage of organic matter in sediments are given in Table 2. The pH of the sediment in all sites was acidic .The highest mean pH was at site 15 with pH value of 5.16, from a range of 4.81 to 5.49. The lowest mean pH was at site 7 at pH 4.15 with values ranging from 4.01 to 4.25.

The highest mean percentage of organic matter measured was at sampling site 15 with a value of 31.78, with readings ranging from 28.20 to 34.20. The lowest mean percentage of organic matter was measured at site 4 at 13.80, with values ranging from 13.00 to 15.60. The mean organic matter in sediments exceeded 13% at all sampling sites

Heavy metal concentration in sediment

The sequential extraction procedure used in this study was based on defined fractions: exchangeable, acid reduction, oxidation, and residual. Concentration of cadmium, copper and lead in sequential extraction of sediments are shown in Tables 3, 4, and 5.

Cadmium concentration in sediment

Concentration of cadmium in sequential extraction of sediments is shown in Table 3. The concentration of cadmium at easily and exchangeable phase at site 11 was the highest among the sites with a mean value of 0.31 μg g^{-1}, its values ranging from 0.23 to 0.35 μg g^{-1}. The lowest concentration of cadmium was at site 4 with a mean value of 0.04 μg g^{-1} (values ranging from 0.02 to 0.07 μg g^{-1}). The highest mean concentration of cadmium at acid reduction phase was measured at

Table 1 Means, SD and ranges of heavy metal concentrations (μg l^{-1}) in water from 15 sites in Tasik Chini

Site	Cd			Cu			Pb		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
1	0.10	0.67	0.02–0.16	4.52	3.16	2.20–8.92	11.72	7.94	4.50–22.89
2	0.12	0.11	0.20–0.26	8.36	12.1	1.10–26.36	5.61	5.04	1.82–13.03
3	0.08	0.10	0.01–0.23	3.04	2.08	0.90–5.08	18.7	25.8	1.70–57.00
4	0.07	0.08	0.01–0.19	3.32	2.64	0.80–6.80	5.92	2.45	2.25–7.24
5	0.07	0.06	0.01–0.14	5.17	6.17	0.75–14.17	6.19	5.04	2.39–13.30
6	0.10	0.11	0.02–0.27	2.68	1.22	1.90–4.50	4.37	2.23	2.52–7.61
7	0.26	0.37	0.01–0.80	7.15	9.07	1.10–20.51	15.18	16.8	6.52–40.38
8	0.05	0.07	0.01–0.16	2.14	1.44	1.15–4.25	3.58	1.69	1.81–5.75
9	0.32	0.48	0.04–1.04	4.68	4.43	1.00–10.11	12.79	15.03	4.32–35.30
10	0.09	0.07	0.04–0.19	2.76	1.88	1.00–4.85	3.85	2.01	1.82–6.62
11	0.12	0.09	0.04–0.25	1.87	0.9	0.99–3.12	4.91	4.41	2.10–11.45
12	0.07	0.04	0.01–0.11	1.77	0.97	0.95–3.180	2.85	1.50	1.72–4.96
13	0.06	0.04	0.01–0.10	5.67	3.7	1.00–16.72	4.62	1.55	2.32–5.61
14	0.08	0.04	0.02–0.12	1.50	0.81	0.65–2.60	7.18	5.30	3.65–15.07
15	0.08	0.05	0.02–0.14	2.22	1.52	1.15–4.47	5.58	3.95	2.12–10.62

Table 2 Mean levels of pH and percentage of organic matter (%) at 15 sites in Tasik Chini

Site	pH			Percentage of organic matter (%)		
	Mean	SD	Range	Mean	SD	Range
1	4.46	0.14	4.30–4.65	25.95	5.10	21.00–33.00
2	4.50	0.42	4.22–5.12	15.75	1.52	14.20–17.50
3	4.35	0.22	4.15–4.59	20.40	3.83	17.40–25.50
4	4.33	0.27	4.12–4.73	13.80	1.23	13.00–15.60
5	4.32	0.43	4.09–4.98	27.90	3.02	23.60–30.00
6	4.56	0.36	4.25–5.08	18.63	4.46	12.00–21.70
7	4.15	0.11	4.01–4.25	18.05	0.90	16.80–18.80
8	4.31	0.27	4.05–4.70	23.20	1.41	21.40–24.80
9	4.21	0.1	4.11–4.34	23.95	3.60	20.00–27.00
10	4.20	0.21	4.07–4.52	22.62	0.79	21.70–23.60
11	4.46	0.22	4.13–4.58	18.80	3.73	14.00–23.00
12	4.53	0.36	4.22–5.02	16.30	5.20	10.00–21.40
13	4.76	0.21	4.52–5.03	16.75	3.35	11.80–19.20
14	4.89	0.06	4.80–4.93	26.23	3.13	22.50–30.00
15	5.16	0.31	4.81–5.49	31.78	2.95	28.20–34.20

site 11 at 0.39 μg g^{-1} (values ranging from 0.28 to 0.52 μg g^{-1}). The lowest mean concentration of cadmium was measured at site 5 at 0.10 μg g^{-1}, (values ranged from 0.05 to 0.15 μg g^{-1}). The highest mean concentration of cadmium at organic oxidation phase was measured at site 15 at 0.53 μg g^{-1}, with values ranging from 0.45 to 0.70 μg g^{-1}, while the lowest mean concentration of it was measured at site 4 at 0.21 μg g^{-1}, with values ranging from 0.10 to 0.45 μg g^{-1}. The concentration of cadmium in the residual phase was noticeably high at site 12 relative to the other stations with a mean value of 0.56 μg g^{-1}, with values ranging from 0.45 to 0.72 μg g^{-1}. The lowest cadmium concentration was at site 2 with a mean value of 0.37 μg g^{-1}, from its range of 0.31 to 0.48 μg g^{-1}.

Copper concentration in sediment

Concentration of copper in sequential extraction of sediments is shown in Table 4. The concentration of

Table 3 Means, SD and range concentrations (μg g^{-1}) of Cd in sediment at 15 sites in Tasik Chini

Site	Exchangeable fraction			Acid reduction fraction			Oxidation fraction			Residual fraction		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
1	0.05	0.023	0.03–0.08	0.14	0.05	0.07–0.18	0.26	0.095	0.16–0.39	0.38	0.059	0.31–0.45
2	0.05	0.025	0.02–0.08	0.11	0.04	0.06–0.16	0.29	0.066	0.22–0.37	0.37	0.073	0.31–0.48
3	0.06	0.029	0.03–0.10	0.14	0.05	0.10–0.22	0.31	0.150	0.12–0.49	0.41	0.071	0.33–0.49
4	0.04	0.020	0.02–0.07	0.11	0.04	0.07–0.15	0.21	0.156	0.10–0.45	0.40	0.542	0.36–0.48
5	0.06	0.031	0.02–0.09	0.10	0.05	0.05–0.17	0.32	0.156	0.10–0.45	0.38	0.090	0.27–0.49
6	0.06	0.031	0.02–0.09	0.11	0.06	0.06–0.20	0.31	0.078	0.21–0.40	0.40	0.057	0.32–0.45
7	0.13	0.077	0.04–0.22	0.15	0.06	0.08–0.23	0.28	0.130	0.12–0.42	0.43	0.129	0.28–0.59
8	0.14	0.085	0.04–0.25	0.27	0.13	0.10–0.40	0.38	0.085	0.31–0.50	0.48	0.153	0.32–0.65
9	0.19	0.104	0.07–0.30	0.24	0.12	0.10–0.38	0.35	0.117	0.18–0.45	0.45	0.115	0.30–0.58
10	0.28	0.156	0.15–0.51	0.37	0.15	0.24–0.59	0.45	0.08	0.35–0.53	0.49	0.089	0.36–0.55
11	0.31	0.066	0.23–0.35	0.39	0.10	0.28–0.52	0.51	0.141	0.30–0.60	0.44	0.117	0.31–0.58
12	0.30	0.078	0.20–0.37	0.37	0.09	0.25–0.46	0.43	0.135	0.34–0.63	0.56	0.119	0.45–0.72
13	0.16	0.066	0.10–0.25	0.24	0.07	0.18–0.34	0.47	0.047	0.41–0.52	0.45	0.114	0.32–0.56
14	0.13	0.096	0.05–0.27	0.26	0.11	0.20–0.42	0.36	0.094	0.25–0.47	0.39	0.127	0.24–0.54
15	0.09	0.023	0.05–0.10	0.17	0.07	0.10–0.27	0.53	0.115	0.45–0.70	0.49	0.125	0.32–0.62

Table 4 Means, SD and range concentrations (μg g^{-1}) of Cu in sediment at 15 sites in Tasik Chini

Site	Exchangeable fraction			Acid reduction fraction			Oxidation fraction			Residual fraction		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
1	0.16	0.062	0.11–0.25	0.08	0.042	0.04–0.14	10.66	0.37	10.33–11.18	8.82	2.82	5.17–11.74
2	0.23	0.082	0.14–0.32	0.11	0.055	0.06–0.19	5.83	1.60	4.25–8.05	8.16	2.86	4.56–11.30
3	0.21	0.054	0.14–0.27	0.09	0.055	0.05–0.16	5.53	1.56	4.15–7.78	11.48	3.47	7.19–15.62
4	0.33	0.190	0.12–0.52	0.10	0.038	0.05–0.14	4.73	2.01	2.44–7.24	8.20	1.57	6.80–9.93
5	0.35	0.211	0.14–0.57	0.11	0.042	0.07–0.16	14.99	1.48	12.85–16.20	10.33	2.36	7.50–12.95
6	0.28	0.117	0.15–0.40	0.09	0.012	0.07–0.10	8.50	1.34	6.50–9.28	11.82	3.61	7.50–14.90
7	0.49	0.265	0.23–0.75	0.14	0.043	0.10–0.19	9.80	1.08	8.92–11.35	8.96	3.93	3.45–12.73
8	0.46	0.250	0.18–0.69	0.14	0.008	0.13–0.15	7.24	0.47	6.70–7.75	9.07	2.63	5.27–11.15
9	0.52	0.259	0.28–0.78	0.17	0.051	0.12–0.24	6.82	2.77	4.25–10.75	9.65	3.78	4.14–12.15
10	0.66	0.383	0.31–1.03	0.22	0.061	0.15–0.30	9.18	3.12	5.20–12.27	12.59	4.44	6.00–15.62
11	0.36	0.095	0.25–0.46	0.16	0.086	0.03–0.22	8.87	2.35	6.10–11.76	8.81	2.96	4.52–10.95
12	0.43	0.214	0.17–0.62	0.17	0.0.6	0.10–0.25	9.71	1.37	8.02–11.07	10.78	4.56	4.72–15.54
13	0.33	0.119	0.18–0.45	0.20	0.070	0.13–0.30	8.88	1.92	6.73–10.95	9.66	1.88	7.62–12.17
14	0.34	0.097	0.20–0.41	0.20	0.085	0.07–0.25	14.67	1.65	12.25–15.95	10.46	1.60	8.20–12.00
15	0.38	0.105	0.24–0.47	0.22	0.119	0.06–0.35	15.64	4.17	12.71–21.76	12.00	3.33	8.27–14.97

copper at easily and exchangeable phase at site 10 was the highest among the sites with a mean value of 0.66 μg g^{-1}, and values ranging from 0.31 to 1.03 μg g^{-1}. The lowest copper concentration was at site 1, with mean value of 0.16 μg g^{-1}, based on its range from 0.11 to 0.25 μg g^{-1}. Sampling sites 10 and 15 recorded high copper concentration at acid reduction phase relative to the other sites with values at 0.22 μg g^{-1} (the respective values ranging from 0.15 to 0.30 μg g^{-1} and from 0.06 to 0.35 μg g^{-1}). The lowest mean concentration of copper at acid reduction phase was measured at site 1 at 0.08 μg g^{-1}. The concentration of copper from the organic oxidation fraction at site 15 was highest among the sites and among all fractions with a mean value of 15.64 μg g^{-1}, while the lowest concentration was at site 4 with a mean value of 4.73 μg g^{-1}. The highest mean concentration of copper at residual phase was measured at site 10 with a mean value of 12.59 μg g^{-1} (values ranging from 6.00 to 15.62 μg g^{-1}), while the lowest mean concentration was recorded at site 2 at 8.16 μg g^{-1} (its values ranging from 4.56 to 11.30 μg g^{-1}).

Table 5 Means, SD and range concentrations (μg g^{-1}) of Pb in sediment at 15 sites in Tasik Chini

Site	Exchangeable fraction			Acid reduction fraction			Oxidation fraction			Residual fraction		
	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range	Mean	SD	Range
1	1.39	0.35	1.05–1.85	1.16	0.17	1.00–1.35	22.2	4.78	18.70–28.85	24.27	7.06	17.69–32.00
2	1.25	0.37	1.00–1.80	1.34	0.45	0.70–1.65	20.85	4.80	13.75–24.00	24.39	7.30	17.07–32.12
3	1.66	0.77	0.85–2.40	1.76	0.44	1.25–2.25	28.26	9.24	18.20–40.10	29.39	7.67	19.70–37.69
4	1.05	0.51	0.55–1.75	1.10	0.41	0.80–1.70	14.00	1.38	12.15–15.50	23.65	6.37	17.92–30.60
5	2.31	1.03	1.45–3.70	1.18	0.43	0.55–1.50	23.24	4.87	17.20–29.00	24.74	11.70	10.44–38.50
6	1.58	0.95	0.95–2.95	0.90	0.25	0.60–1.15	18.49	4.43	14.30–24.60	24.50	5.44	17.41–29.00
7	1.18	0.49	0.60–1.75	1.14	0.53	0.35–1.50	14.00	1.31	12.55–15.50	23.31	4.87	18.33–30.00
8	1.31	0.39	0.80–1.75	0.99	0.49	0.35–1.55	15.33	1.12	14.35–16.95	28.86	8.55	17.43–37.25
9	1.25	0.27	1.25–1.85	0.83	0.44	0.20–1.20	14.28	1.08	13.10–15.50	25.71	6.08	17.10–31.41
10	1.29	0.29	1.00–1.70	0.96	0.50	0.60–1.70	14.52	1.87	13.00–17.05	25.39	6.38	17.04–32.42
11	1.49	0.62	0.90–2.05	0.94	0.38	0.40–1.30	16.40	1.63	15.25–18.80	26.88	6.07	18.30–32.50
12	1.95	0.37	1.40–2.25	1.11	0.49	0.65–1.80	14.04	0.99	13.10 –15.35	31.19	9.80	21.00–44.22
13	1.97	0.47	1.50–2.60	1.75	0.50	1.35–2.45	24.61	5.57	18.35–31.50	31.26	6.81	24.26–40.52
14	2.95	0.73	2.25–3.95	1.88	0.87	0.70–2.70	28.08	3.64	27.20–35.15	27.20	6.92	20.45–35.00
15	3.65	0.50	2.90–3.95	2.00	0.19	1.75–2.20	31.83	5.31	28.45–38.75	32.55	6.49	25.43–38.92

Table 6 Kruskal–Wallis test (X^2) of Cd, Cu and Pb concentration in water at 15 sampling sites

Element	X^2	*df*	*p*
Cd	6.30	14	ns
Cu	7.87	14	ns
Pb	16.74	14	ns

p: significant level, *ns*: not significant

Lead concentration in sediment

Concentration of lead in sequential extraction of sediments is shown in Table 5. The concentration of lead at easily and exchangeable phase at site 15 was the highest with a mean value of 3.65 μg g^{-1}, the value ranging from 2.90 to 3.95 μg g^{-1}. The lowest lead concentration was at site 4 with a mean value of 1.05 μg g^{-1}, value ranging from 0.55 to 1.75 μg g^{-1}. The highest mean concentration of lead at acid reduction phase was measured at site 15 at 2.00 μg g^{-1}, where value ranges from 1.75 to 2.20 μg g^{-1}. The lowest mean concentration of lead in similar fraction was noted at site 9 with a mean value at 0.83 μg g^{-1}, (its value ranging from 0.20 to 1.20 μg g^{-1}). The concentration of lead at organic oxidation phase at site 15 was the greatest among the sites and among all fractions with a mean value of 31.83 μg g^{-1}, ranging from 28.45 to 38.75 μg g^{-1} while the concentration of it at site 4 and 7 were the lowest among the sites with a mean value of 14.00 μg g^{-1}, ranging from 12.15 to 15.50 μg g^{-1} and from 12.55 to 15.50 μg g^{-1} respectively. The highest mean concentration of lead at residual phase was measured at site 15 with a mean value of 32.55 μg g^{-1}, ranging from 25.43 to 38.92 μg g^{-1} while the lowest mean concentration of it was measured at site 1 at 24.27 μg g^{-1}, ranging from 17.69 to 32.00 μg g^{-1}.

Comparison between sampling sites in water and sediment

Comparison between sampling sites using Kruskal–Wallis test showed that there was no significant differences for cadmium, copper and lead concentration in water at 15 sampling sites (Table 6). In sediment, comparison between sampling sites using one-way analysis of variance showed that there were significant differences at exchangeable fraction for cadmium, and lead while there was no significant differences for copper (Table 7). At acid reduction fraction and oxidation fraction, comparison between sampling sites showed that there were significant differences for cadmium, copper and leads while there was no significant difference at residual fraction.

Individual contamination factor

The individual contamination factor (ICF) for three heavy metals in this study is shown in Table 8. The

Table7 Statistical variation (ANOVA) of Cd, Cu and Pb concentration in sediment at 15 sampling sites

Element/sediment fractions	SS_b	*df*	MS_b	SS_w	*df*	MS_w	*F*	*p*
Cd								
Exchangeable	0.472	14	0.034	0.234	45	0.005	6.49	<0.001
Acid reduction	0.599	14	0.043	0.342	45	0.008	5.62	<0.001
Organic oxidation	0.502	14	0.036	0.538	45	0.012	3.00	<0.01
Residual	0.162	14	0.012	0.475	45	0.011	1.09	ns
Cu								
Exchangeable	0.930	14	0.066	1.63	45	0.036	1.83	ns
Acid reduction	0.136	14	0.010	0.17	45	0.004	2.46	<0.05
Organic oxidation	647.4	14	46.24	189	45	4.21	10.9	<0.001
Residual	114.4	14	8.20	471	45	10.2	0.80	ns
Pb								
Exchangeable	28.9	14	2.07	15.5	45	0.35	6.00	<0.001
Acid reduction	8.4	14	0.60	9.75	45	0.22	2.77	<0.01
Organic oxidation	2155	14	154.0	679	45	15.1	10.2	<0.001
Residual	521	14	37.2	2,438	45	54.2	0.69	ns

p: significant level, *ns*: not significant, SS_b: sum of squares between groups, MS_b: mean squares between groups, SS_w: sum of squares within groups, MS_w: mean squares within groups

Table 8 Individual contamination factors (ICF) of 3 elements at 15 sites in Tasik Chini

Site	ICF (Cd)	ICF (Cu)	ICF (Pb)
1	1.18	1.23	1.1
2	1.21	0.75	0.96
3	1.43	0.51	1.10
4	0.90	0.63	0.68
5	1.26	1.49	1.08
6	1.20	0.75	0.85
7	1.56	1.16	0.70
8	1.64	0.86	0.62
9	1.73	0.78	0.64
10	2.53	0.80	0.66
11	2.70	1.06	0.70
12	1.94	1.04	0.55
13	1.91	0.97	0.90
14	1.92	1.45	1.28
15	1.59	1.35	1.17

individual contamination factor for the various sampling sites were calculated from the results of fractionation by dividing the sum of the first three fractions (i.e. loosely and exchangeable, acid reduction and organic oxidation forms) by the residual fraction for each site (Ikem et al. 2003). The highest level of individual contamination factor for cadmium was calculated at site 11 with a value of 2.7, while the lowest level of it was calculated at site 4 with a value of 0.9. The highest level of individual contamination factor for copper was calculated at site 5 with a value of 1.49, while the lowest level of it was calculated at site 3 with a value of 0.51. The highest and lowest levels of individual contamination factor for lead were calculated at site 14 and 12 with a value of 1.28 and 0.55 respectively.

Discussion

The heavy metal concentration in water at all sampling sites occurs in descending order of Pb > Cu > Cd, except for sampling sites 2 and 13 where copper concentration was higher than lead and cadmium. The elevated concentrations of lead were thought to be associated with boating ecotourism activities in the lake. An obvious potential contributor of lead to the water is boating activities (Byrd and Perona 1980). The high concentrations of cadmium in water at sampling sites 7 and 9, seems to corresponds to low pH sediment in the former site while the latter site showed agricultural runoff entering lake. The higher concentrations of copper were noticeable at sampling sites 2 and 7, while the most polluted heavy metal at sampling sites 3 and 7 is lead. Similarly, the high concentration of lead at site 3 was situated at the boat stations where high boating activities takes place and site 7 was located where the pH of the sediment was the lowest. Byrd and Perona (1980) have showed that the highest concentration of lead was found in the Turlok Lake when there were high boating activities.

It is established that due to low pH, heavy metals may be desorbed from the sediment into water in Tasik Chini. Samecka-Cymerman and Kempers (2001) have showed that the highest concentrations of cadmium, copper and lead in water were found in lakes which had the lowest water pH and the lowest sediment pH. Tokalioglu et al. (2000) have indicated that cadmium, copper and lead concentrations in the lake water samples, decreased with increasing pH, because the metal binding abilities are decreased with decreasing pH due to proton binding. A decrease in pH will increase the competition between metals and hydrogen ions for binding sites and may dissolve metal complexes, releasing free metal ions into the water column (Elith and Garwood 2001). An increase in pH is generally accompanied by a decrease of the solubility of many toxic heavy metals in water (Avila-Pèrez et al. 1999). Correlation analysis also showed relationship between individual elements including Cu and Pb (r=0.30), Pb and Cd (r=0.12) and between Cd and Cu (r=0.46). Pearson correlation showed that there was no significant correlation among these metals (p>0.05).

Sequential extraction results can provide information on possible chemical forms of heavy metals in sediments (Xiangdong et al. 2000). The effects of heavy metals in the environment depend to a large extent on whether they occur in forms that can be taken up by plants or animals. According to Elith and Garwood (2001), lead maybe strongly adsorbed onto sediment particles and therefore largely unavailable, while cadmium ions can be directly absorbed to water and it is known to be most mobile among the other metals (Kabata-Pendias and Pendias 2001). A wide range of values for heavy metal concentrations was observed for the sediments. On the average, the percentage of cadmium associated with different fractions in the sediment from all sites was in the order of residual (37.2%) > organic matter (32%) > acid reduction (18.41%) > easily and exchangeable (12.39%). The percentage of copper from all sites was in the order of residual (50.3%) > organic matter (47.1) > easily and exchangeable (1.8%) > acid reduction (0.8%). The percentage of lead was in the order of residual (53.4%) > organic matter (40.6%) > easily and exchangeable (3.5%) > acid reduction (2.5%). Assuming that bioavailability is related to solubility, then metal bioavailability decreases in the order of exchangeable forms > acid reduction forms > organic forms > residual forms (Ma and Rao 1997; Xiangdong et al. 2000). The residual forms are not expected to be released under normal conditions in nature (Dean 2002) and could be considered as an inert phase (Xiangdong et al. 2000).

Besides metal concentrations, metal availability is also influenced by other characteristics of the soil/sediment system such as pH and organic matter content, which control the solubility and therefore the availability of metals (Vogel-Mikus et al. 2005). Among the non-residual fractions, the organic matter fraction was much higher than other fractions in all sites. The percentage of cadmium in the non-residual fractions was greater than the residual fraction. About 63% of the cadmium in sediment was associated with the exchangeable, acid reduction and oxidation fractions. Forstner (1985) reported that cadmium was characteristically enriched in the more mobile fractions and more mobile than most of other heavy metals (Kong and Liu 1995). The present results indicate that cadmium and lead have greater potential for mobilization from the sediments than copper because of their higher concentration at the acid reduction fraction.

Results of organic matter analysis showed that the levels of organic matter present in sediment samples varied throughout the lake and all sampling sites were relatively rich in organic matter. It is assumed that such differences were related to variations in the quantity and sources of organic matter present at each site and the ability of organic matter to move in the sediments. It is likely that the high levels of organic matter present in sites 1, 5, 14 and 15 are results of accumulating over time of organic input from the hinterland of the lake area and decomposition of organic matter. Organic matter has a high specific storage capacity for heavy metals (Elith and Garwood 2001). Acidic pH condition is known to influence the sorption of lead by organic matter fraction in sediments (Ikem et al. 2003). Analysis of pH and percentage of organic matter present in sediments concluded that there were strong correlations between each of these factors and the concentrations of copper and lead. Results showed that the concentration of heavy metals at oxidation fraction increased with increasing pH levels and percentage of organic matter present in the sediments.

The presence of organic matter may increase the levels of lead and copper in the organically bounded form (Kong and Liu 1995). The results of this study similarly showed that with an increase in organic matter and pH in the lake sediment sample within the lake followed with an increase in the concentration of Cu and Pb at oxidation fraction. Copper can easily form complexes with organic matters due to its high formation constants forming organic-copper compounds (Xiangdong et al. 2000; Preda and Cox 2002; Wang et al. 2004) and these are mainly bound to the organic matter fraction (Fernandes 1997; Kabata-Pendias and Pendias 2001; Pagnanelli et al. 2004). Under oxidizing conditions, metals present in both natural organic matter and living organisms (as a result of bioaccumulation of metals) may be remobilized into the aquatic environment (Ikem et al. 2003). In aquatic systems, the distribution of copper is mainly affected by natural organic matter such as humic materials and amino acids (Xiangdong et al. 2000). The first two fractions, i.e., the exchangeable and acid reduction fractions were found to be minor contributors for copper. In the present study low copper content in these two fractions indicates that copper maybe less bioavailable in the sediments. There was a significant relationship between copper bound to the organic fraction and sediment organic contents. Thus, it can be suggested that if a significant amount of organic matter is present, the availability and consequently the toxicity of the element will be drastically reduced (Fernandes 1997).

A Pearson correlation was carried out between organic matter percentages, pH and concentration of cadmium, copper and lead at the oxidation fraction. There was no significant correlation between concentration of cadmium with organic matter percentage and pH ($p>0.05$). Cadmium is most mobile in acid soils/sediments within the range of pH 4.5 to 5.5, and the solubility of it is closely related to the acidity of the soil/sediments solution. With regard to levels of pH, cadmium maybe desorbed from the sediment into water in Tasik Chini. The result of Pearson correlation (r) for organic matter for copper was 0.75 ($p<0.001$), which means that there was a strong linear correlation with organic matter. There was a linear correlation between lead and the percentage of organic matter in the sediment ($r=0.55$ and $p<0.05$). Thus, organic matter shows a significant to bind copper and lead the sediment in Tasik Chini. There was a linear correlation between copper and pH ($r=0.56$ and $p<0.05$) and lead and pH ($r=0.74$ and $p<0.01$).

At exchangeable fraction, there were significant differences for cadmium between sampling sites 1, 2, 3, 4, 5, 6 and sampling sites 10, 11, 12. Cadmium concentration was also significantly different between sampling sites 10, 11, 12 and sampling site 15. For lead significant differences were observed between sampling sites 3, 6, 9, 11, 12, 13 and sampling site 15. Similarly there was a noticeable significant difference between sampling sites 4, 7, 8, 10 and sampling sites 14, 15. In acid reduction fraction, comparison between sampling sites showed that there were significant differences for cadmium, copper and lead. Significant differences for cadmium were observed between sampling sites 1, 2, 3, 4, 5, 6 and sampling sites 10, 11 12; and also between sampling site 10 and sampling site 15.

At oxidation fraction, comparison between sampling sites showed that there were significant differences for cadmium, copper and lead. Significant differences for cadmium were observed between sampling site 4 and sampling sites 11, 15. Significant differences for copper were observed between sampling site 1 and sampling site 4; between sampling sites 2, 3, 4 and sampling sites 5, 14, 15. Other significant differences were also observed between sampling site 5 and sampling sites 6, 8, 9, 10, 11, 12, 13; and also between sampling site 6, 7, 8, 9, 10, 11, 13 and sampling sites 14, 15. Significant differences for lead were observed between sampling site 2 and sampling site 15; between sampling sites 4, 6, 7, 8, 9, 10, 11, 12, 13 and sampling sites 14, 15.

The ICF reflects the risk of contamination of a water body by a pollutant (Ikem et al. 2003). The higher the mobility of the ions within the fractions in the sediments (i.e. exchangeable forms, acid reduction forms and oxidation forms), the higher is the potential risk of water contamination by sediment in the lake. However, oxidation forms are relatively less mobile than those extracted in exchangeable and acid reduction forms because it bound stronger to the sediment components (Kabala and Singh 2001). The remobilization of metals from lake sediment into the water column will be influenced by factors such as pH, chemical forms of the heavy metals, and the physicochemical characteristics of the water column (Ikem et al. 2003). At sites 10 and 11 cadmium showed higher ICF when compared to other sites. Therefore, the risk of cadmium contamination in these two sites was higher than the other sites. Generally, the ICF for cadmium was much higher than of lead and copper; therefore cadmium poses a higher risk to the water in Tasik Chini in comparison to copper and lead.

Conclusion

The heavy metal concentration in the water are described in the descending order of Pb > Cu > Cd at all sampling sites, except for sampling sites 2 and 13 for copper. The present results indicate that cadmium and lead have higher potential for mobilization from the sediment than copper because of their higher concentration at the exchangeable and acid reduction fraction. Among the non-residual fractions, the organic matter fraction is much higher than other fractions in all sites. Analysis of pH and percentage of organic matter present in sediments conclude that there are strong correlations between each of these factors and the concentrations of copper and lead at oxidation fraction. Results of this study also showed that with an increase in organic matter and pH in sediment a similar increase in the concentration of copper and lead occurs at the oxidation fraction. The individual contamination factor (ICF) shows that the risk of cadmium is higher than the risk of copper and lead.

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