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Dissolved Heavy Metals and Water Quality in the Surface Waters of Rivers and Drainages of the West Peninsular Malaysia

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Abstract: The dissolved concentrations of metals (Cd, Cu, Pb, Ni, Fe and Zn), temperature, total dissolved solids, pH, dissolved oxygen, salinity and conductivity were determined in the surface waters of 24 geographical sampling sites including city and urban drainages and rivers, from the west Peninsular Malaysia, collected in January to April 2005. From these sampling sites, the ranges (min-max) of dissolved metal concentrations (mg/L) were Cd: 0.001-0.055, Cu: 0.001-0.1773, Pb: 0.001-1.523, Ni: 0.001-0.246, Fe: 0.001-35.67 and Zn: 0.0001-0.609 while for the water quality are pH: 4.96-9.81, dissolved oxygen (0.39-7.26 mg/L), total dissolved solids (0.002-10.02 mg/L), salinity (0.00-8.93 ppt), conductivity (3.33-17423 μS/cm) and temperature (27.8-35.3°C). Some sites with elevated dissolved concentrations of heavy metals and poor water quality indicated the anthropogenic inputs of industrial and urban wastes. Regular monitoring of water quality in all drainage waters is recommended.

Key words: water quality, dissolved heavy metals, rivers and drainages, west Peninsular Malaysia.

Introduction

Studies on water quality in the aquatic environment are still popular in the evaluation and management of rivers ecosystems in many countries (Parinet et al., 2004b; Owen and Niemeyer, 2005; Njenga, 2004; Nhaphi et al., 2002; Subramanian, 2004; Jayaprakash et al., 2005; Iwashita and Shimamura, 2003) including Malaysia (DOE, 2001, 2004). This is due to the changes in water chemistry of river and drainages can be the results of domestic, industrial or agricultural discharges which may in turn lead to aquatic ecosystem degradation (House, 1990) such as deterioration of water quality in the rivers and drainages. Therefore, the determination of chemical parameters of the water samples can act as indicators of water pollution due to both natural and anthropogenic inputs.

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According to House (1990), accumulation and/or fluctuations of chemical parameter concentrations can serve to highlight potential ecosystem dysfunctions and thereby provide an early warning of possible ecological problems. In Malaysia, studies on water quality in drainages is limited in the literature except for a few studies on rivers (Azlina et al., 2005) and intertidal waters (Yap et al., 2005). According to Said et al. (2004), meeting water quality expectations for streams and rivers is required to protect drinking water resources, encourage recreational activities and to provide a good environment for fish and wildlife. Therefore, monitoring the water quality is of ecotoxicological importance.

Since the goals of most water quality monitoring programmes are to describe the status of water quality of a defined area and to determine the factors that affect the water quality, it is therefore important to know the correlation with other physico-chemical parameters and description of each sampling site. Thus, the objectives of this study were: (1) to determine some physico-chemical parameters including temperature, pH (potential hydrogen), conductivity, dissolved oxygen (DO), total dissolved solids (TDS) and dissolved concentrations of Cd, Cu, Fe, Ni, Pb and Zn, at 24 sampling sites in the intertidal waters of the west coast of Peninsular Malaysia and (2) to find the relationships between all the parameters by using correlation analysis (CA) and multiple stepwise regression analysis (SRA).

Materials and Methods

Surface water samples were collected from 24 sampling sites in some urban and drainages from Kuala Perlis to Johore, Peninsular Malaysia (Figure 1 and Table 1). The physico-chemical characteristics of the water recorded directly in the field at each sampling site were temperature, conductivity, salinity, pH, DO and TDS. These water parameters were determined by using YSI 556 MPS (Multi-Probe System). A total of three replicates

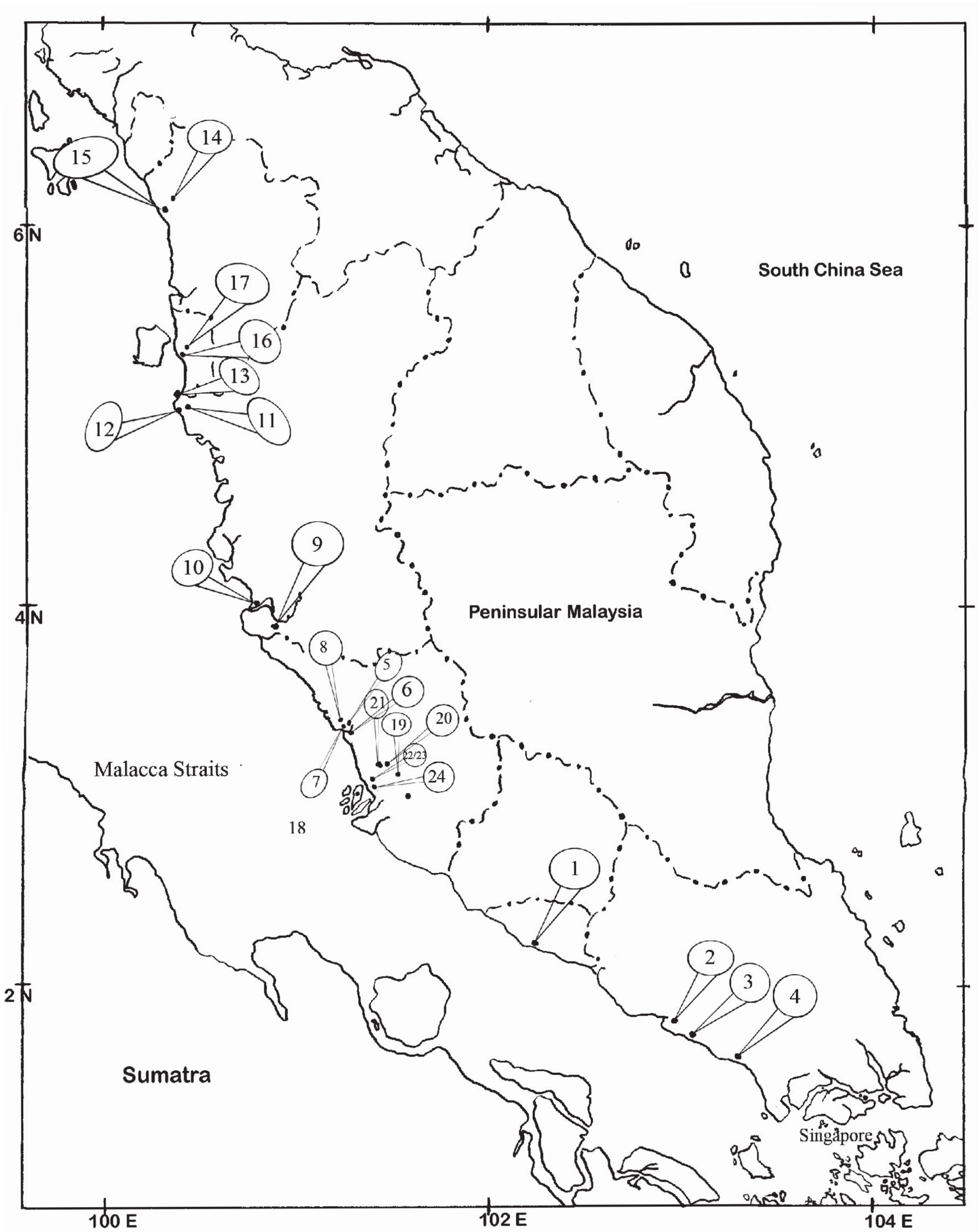

Figure 1: Map showing the sampling sites. Names of sampling sites represented by alphabets follow those in Table 1.

Table 1: Date of sampling and GPS of each sampling site of the city and urban drainages/river waters in the west Peninsular Malaysia

No.	*Sampling sites*	*Date of sampling*	*Longitude*	*Latitude*
1	Jetty Melaka	17.01.05	N 02°11.398′	E 102°14.708′
2	Batu Pahat River	18.01.05	N 01°51.481′	E 102°55.460′
3	Senggarang River	18.01.05	N 01°44.888′	E103°03.181′
4	Benut River	18.01.05	N 01°39.095′	E 103°15.158′
5	Kg. Kuantan (Firefly park)	18.04.05	N 03º21.745′	E 101º18.093′
6	Kg. Penambang	18.04.05	N 03º21.744′	E 101º18.096′
7	Bernam River	18.04.05	N 03º21.599′	E 101º14.965′
8	Hutan Melintang	18.04.05	N 03º52.345′	E 100º55.965′
9	Hutan Melintang Port (Abandoned)	18.04.05	N 03º21.599′	E 101º14.965′
10	Bagan Datoh	18.04.05	N 03º59.563′	E 100º47.150′
11	Kuala Kurau River	19.04.05	N 05º01.052′	E 100º26.017′
12	JlnPantai,Kurau	19.04.05	N 05º01.106′	E 100º24.779′
13	BaganTiang Jetty	19.04.05	N 05º06.702′	E 100º23.840′
14	Alor Setar	20.04.05	N 06º07.420′	E 100º21.595′
15	Kedah River	20.04.05	N 06º06.624′	E 100º17.282′
16	Juru-2 (Juru River)	20.04.05	N 05º19.772′	E 100º26.083′
17	Juru-1 (Packard Bell factory)	20.04.05	N 05º20.105′	E 100º26.011′
18	Serdang-1 (JP Metal factory)	25.04.05	N 05º20.072′	E 100º26.080′
19	Shah Alam-2 (Industrial area)	25.04.05	N 03º02.665′	E 101º32.512′
20	Shah Alam-1 (Jalan Renggam)	25.04.05	N 03º03.683′	E 101º31.173′
21	Klang-3 (Taman Rashna)	25.04.05	N 03º03.684′	E 101º30.347′
22	Klang-2 (Bdr. Sultan Sulaiman)	25.04.05	N 03º01.151′	E 101º22.421′
23	Klang-1 (Jetty of Pengkalan Nelayan)	25.04.05	N 03º01.120′	E 101º22.453′
24	Kapar Besar River	25.04.05	N 03º00.141′	E 101º21.823′

were taken for every parameter. Water samples were collected for the analysis of dissolved concentrations of heavy metals. Upon collection in the field, the water samples were immediately filtered through a filter paper Whatman No. 1 (medium speed) and they were preserved with high purity nitric acid at pH < 2.0. Water samples were kept in acid-washed polyethylene bottles and later into an icebox to prevent sample deterioration during transportation to laboratory. In the laboratory, the samples were stored below 4°C until analysis. To avoid possible contamination, all glassware and equipment used were acid-washed (Yap et al., 2002). Deionised water was used for blank analysis and dissolved heavy metal determination were done by using an air-acetylene atomic absorption spectrophotometer, an inorganic analytic instrument made by Perkin-Elmer™, model AAnalyst800.

A quality control sample was routinely run through during the period of metal analysis. Procedural blanks were prepared and the metal concentrations in the blanks were negligible (Yap et al., 2003). Quality control was also routinely run by checking standard stock solution for Cd, Cu, Ni, Fe, Pb and Zn for every 10 samples to check for accuracy. The recoveries for the three parameters ranged from 90 to 110% and these recoveries were acceptable.

For statistical analysis, data recorded negative values by using AAS were given 0.001 mg/L. All data obtained were analyzed using Statistical Analysis System (SAS) for Windows, Release 6.12. Simple statistical analyses were done based on the untransformed data by using SAS. All the data were transformed by $\log_{10}(x + 1)$ before Spearman's correlation analysis and multiple stepwise regression analysis (SRA). The SRA were carried out to find out the most influential variables affecting the dissolved concentrations of heavy metals of water samples. The independent variables included temperature, conductivity, TDS, salinity, DO, pH and metals other than the metal studied. All the independent variables which met the 0.15 significance level would be selected for entry in the model (SAS, 1987).

Results

From Figure 2, the ranges of dissolved metals were Cd: 0.001-0.055 mg/L, Cu: 0.001-0.1773 mg/L, Pb: 0.001-1.523 mg/L, Ni: 0.001-0.246 mg/L, Fe: 0.001-35.67 mg/L and Zn: 0.0001-0.609 mg/L while for the physico-

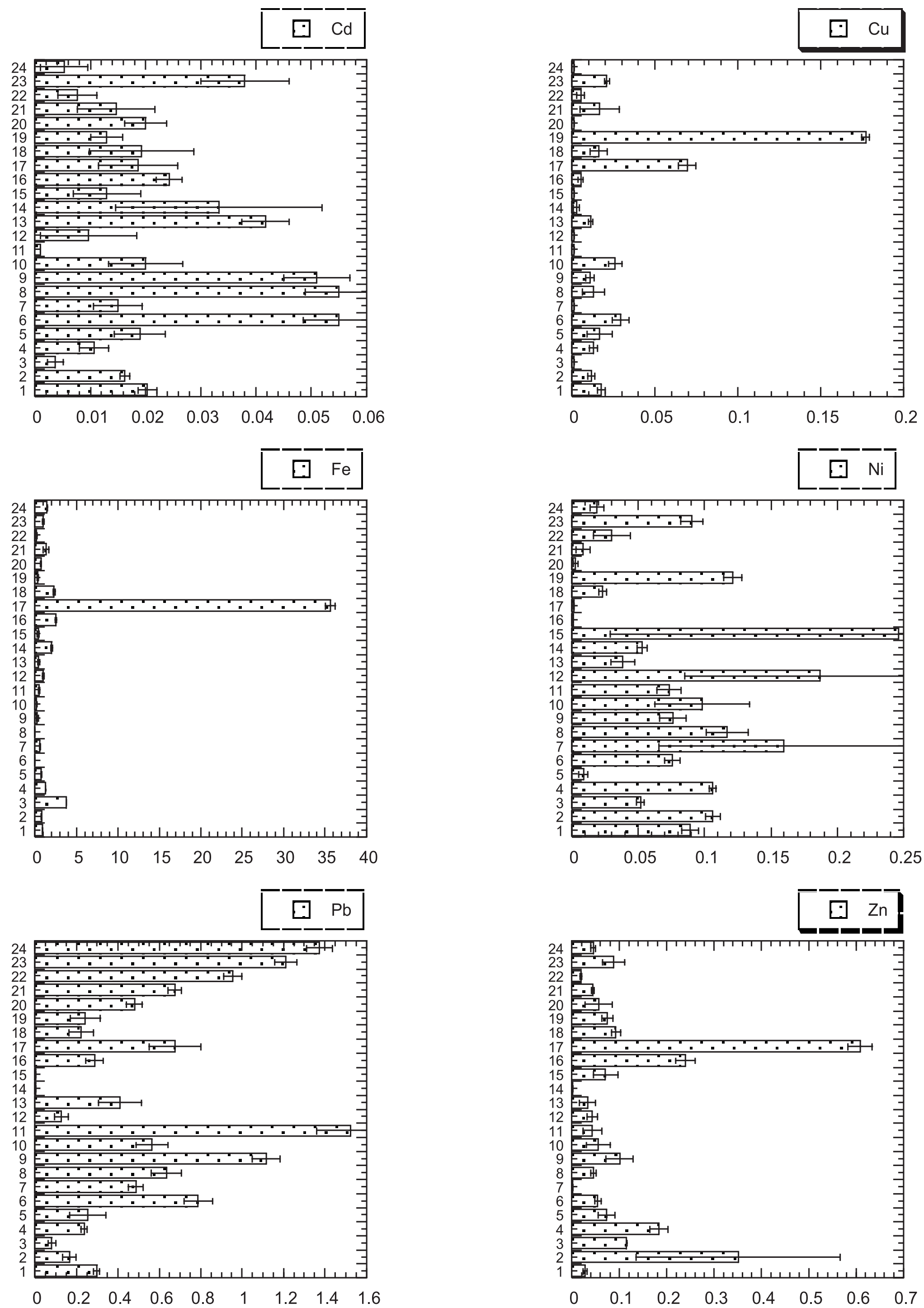

Figure 2: Dissolved concentrations (mean [mg/L] ± standard deviation) of Cd, Cu, Ni, Pb, Fe and Zn in the surface waters of the city and urban drainages/river waters in the west Peninsular Malaysia.

chemical parameters were pH: 4.96-9.81, DO: 0.39-7.26 mg/L, TDS: 0.002-10.02 mg/L, salinity: 0.00-8.93 ppt, conductivity: 3.33-17423 µS/cm and temperature: 27.8-35.3°C.

For the physico-chemical parameters as shown in Figure 3, the lowest temperature was found at Sg. Kapar Besar while the lowest concentration was found at Juru-1. For salinity and conductivity, Pelabuhan Hutan Melintang and Klang-1 were found to record the highest values while most of the sampling sites recorded values below 2 ppt and 2000 µS/cm. For DO, the lowest concentrations were found at Klang-2 while the highest

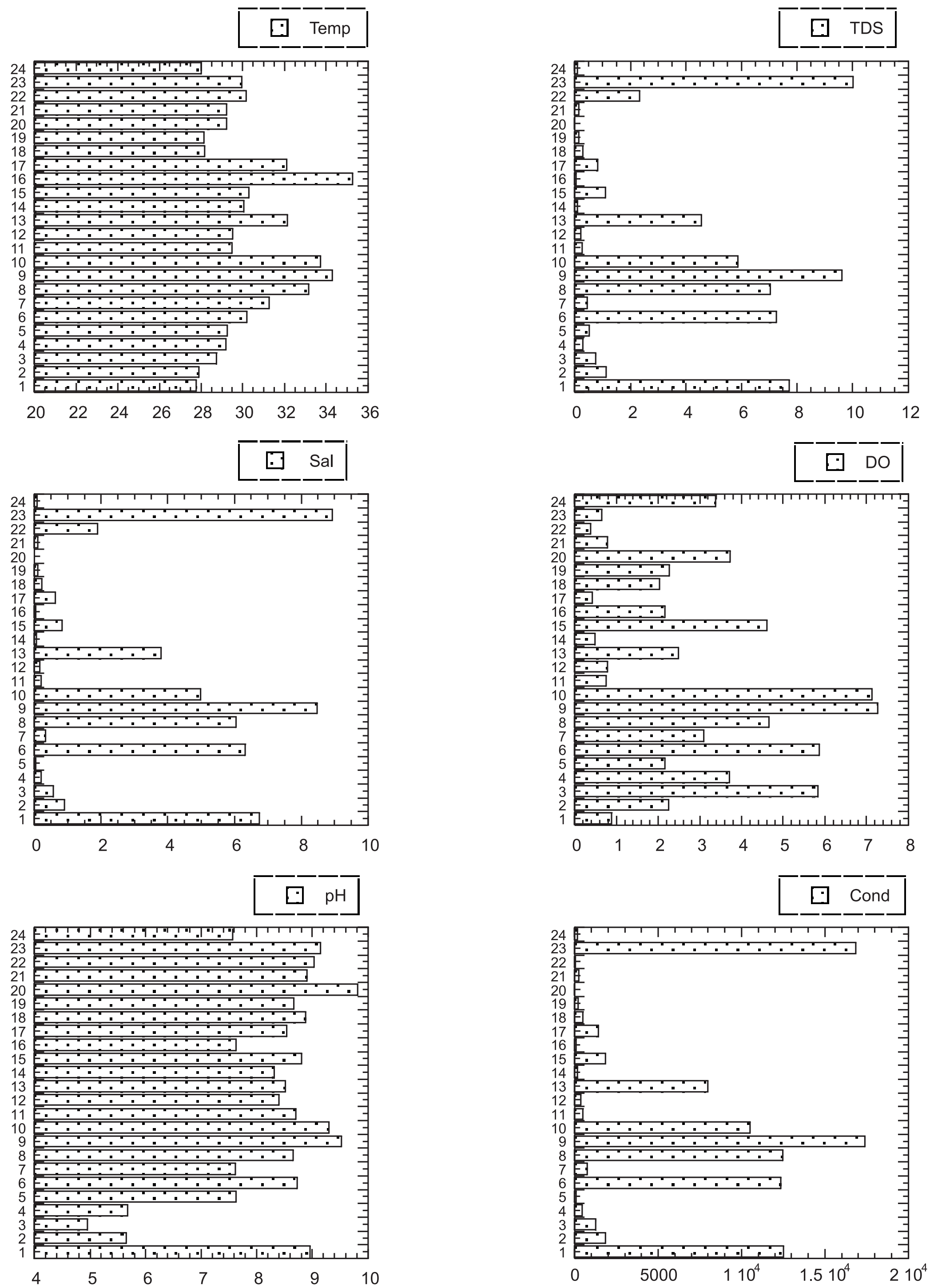

Figure 3: Mean values of temperature (temp; °C), conductivity (cond; µs/cm), total dissolved solids (TDS; mg/L), salinity (sal; ppt), dissolved oxygen (DO; mg/L) and pH of Pb and Zn in the surface waters of the city and urban drainages in the west Peninsular Malaysia.

value was Pelabuhan Hutan Melintang (that could be due to tidal interchange; therefore high mixing and aeration at the surface water is high). As reviewed by Hynes (1971), deoxygenated waters (low DO) is usually caused by bacterial breakdown of organic matter, but it may be due to other reducing agents. With the organic effluents, the amount of DO in the polluted waters of rivers and drainages falls more gradually. The oxygen can only be replaced by aeration at the water surface or by the photosynthetic activities of green plants.

For pH, as reviewed by Hynes (1971), the pH of water has effects in its own right, and pH values of below 5 units or above 9 are definitely harmful to most animals. In this study, Sg. Senggarang was recorded to have pH below 5 while Shah Alam-1, Hutan Melintangf Port and Bagan Datoh were recorded to exceed pH 9. Ammonia is much more toxic in alkaline than acidic waters because its unionized form (NH_3) is more toxic than the ion NH_4^+ (Hynes, 1971).

For TDS, the lowest concentrations were found at Shah Alam-2 and Juru-2 while the highest value was found at Klang-1. For TDS, all the values were below the Malaysian Interim Marine Water Quality Standard of 50 mg/L and 1500 mg/L for Malaysian National Guidelines for Drinking Water Quality (DOE, 2001). The highest levels of TDS were also quantified in the Juru-2 (10.02 mg/L) water was very low when compared to the TDS value as suggested by the US EPA namely a maximum level of 250 mg/L to minimize harm to humans and aquatic life (US EPA, 2002). Although the ranges of TDS concentrations are natural within aquatic systems, the high values observed in some sites are likely due to anthropogenic wastewater releases by local residents or industry.

The lowest dissolved Cd concentration was found at Sg. Kuala Kurau while there are six sites which exceeded 0.03 mg Cd/L. These sites are Klang-1 (industrial area), Bandar Alor Setar (urban and highway), Bagan Tiang Jetty (receiving pesticides runoff from paddy field and plantations) while the abandoned port at Hutan Melintang Port received unknown anthropogenic sources and Kg. Penambang received domestic wastes including detergents since it is close to a restaurant. For Cu, very obvious pattern was found in which Shah Alam-2 and Juru-1 exceeded 0.050 mg/L while other sites were below 0.05 mg/L. The elevated dissolved Cu levels at the sampling sites are mostly related to industrial activities in the surrounding since Juru-1 is close to an electronic factory while Shah Alam-2 is close to an industrial area too.

The lowest dissolved Fe concentration (35.7 mg/L) was found at Juru-1 while the highest concentrations of other sites were all below 5.0 mg/L. For Fe, although Fe is not a known anthropogenic metal, the significant elevated concentration of Fe at Juru-1 signified the anthropogenic source for this metal into the drainage nearby. This dissolved Fe concentration is comparable to the most polluted site reported for Oder River at Wroclaw (14.6 mg/L) (Dojlido and Best, 1993). For Ni, there are three sites which exceeded 0.15 mg/L namely Sg. Kedah (that received urban wastes), Jalan Pantai Kurau (that received agricultural runoff or pesticides) and Sg. Bernam (that received agricultural runoff). The highest Ni concentration found at Sg. Kedah (0.246 mg/L) was within the polluted water reported for Sirava reservoir (0.001-1.075 mg/L) in the former Czechoslovakia (Florian et al., 1983). Moore and Ramamoorthy (1984) reported that values of 0.003-0.100 mg Ni/L for rain in industrialized areas, reaching 2.00 mg/L in the vicinity of the nickel smelter at Sudbury in Canada.

For Pb, there are four sites exceeding 1.00 mg Pb/L namely Sg. Kapar Besar, Klang-1, Kurau Town and Hutan Melintang Port. The first three sites are related to the observable activities at the sampling sites namely urban and small industrial activities such as motor workshops/ repairs. The lowest dissolved Pb concentrations were found at Sg. Kedah and Bandar Alor Setar.

For Zn, Juru-1, Juru-2 and Sg. Batu Pahat exceeded 0.20 mg/L. This again is related to the industrial activities of the surrounding area. According to Mance and Yates (1984), domestic sewage may typically contain 0.20 mg/ L. Polprasert (1982) reported 0.01-0.178 mg/L for Zn in the Chao Phraya River in Thailand. The lowest dissolved Zn concentrations were found at Sg. Kedah and Sg. Bernam while the highest concentration was found at Juru-1.

The concentrations of dissolved metals in the water samples collected from urban and drainages could be most likely due to human activities of the sampling sites. Pb was present in the canal water at each of the sites, ranging from 0.001 to 1.523 mg/L. Except for sites at Sg. Kedah and Bandar Alor Setar, Pb concentrations of other sampling sites exceeded the EPA Criteria for Continuous Concentration (CCC) (human health (organism + water) criteria) value (0.0025 mg/L) and were also above the USEPA Criteria Maximum Concentration (CMC) (human health criteria) level (0.065 mg/L) (USEPA, 2002). Except for nine sampling sites, Ni concentrations for other sampling sites exceeded the USEPA CCC value for Ni (0.052mg/L) but sites had Ni concentrations lower than the USEPA CMC (0.47mg/L) (USEPA, 2002).

The highest concentrations of both Pb and Ni, designated as priority pollutants in surface water by the USEPA, were found at sampling sites close to human activity. The dissolved Cu concentration recorded at all sampling sites exceeded the USEPA CCC (0.009 mg/L) and CMC (0.013 mg/L) levels significantly (USEPA, 2002). The significant elevated concentration of Cu was found at Shah Alam-2 and Juru industrial area.

Correlation matrix analysis of the physico-chemical parameters and dissolved concentrations of heavy metals are shown in Table 2 while the most influential parameters affecting the dissolved concentrations of each metal by using multiple linear stepwise regression analysis are presented in Table 3. Dissolved Cd correlated only weakly (P< 0.05) with dissolved Cu (R = 0.43), temperature (R = 0.48), conductivity (R = 0.47), TDS (R = 0.45) and salinity (R = 0.41). When the relationship is based on SRA, dissolved Cd is significantly influenced by temperature and salinity only (P< 0.001).

Dissolved Cu correlated only weakly (P< 0.05) with TDS (R = 0.41) and this direct correlation is almost supported by not even one parameter selected to be the influential parameter in the SRA. Dissolved Fe correlated negatively and weakly (P< 0.05) with dissolved Ni (R = –0.46), TDS (R = –0.48), salinity (R = –0.46), DO (R = –0.42) and pH (R = –0.44). When the relationship is based on SRA, dissolved Fe is significantly influenced by dissolved Ni and Zn and DO. Dissolved Ni only correlated weakly (P< 0.05) with conductivity (R = 0.46) and salinity (R = 0.41). When the relationship is based on SRA, dissolved Ni is significantly influenced by dissolved Cd, Fe and Pb and conductivity. Dissolved Pb

Table 2: Spearman's correlation coefficients based on $\log_{10}$ transformed data on dissolved metals and water quality (N = 24).

	Cd	*Cu*	*Fe*	*Ni*	*Pb*	*Zn*	*Temp*	*Cond*	*TDS*	*Sal*	*DO*	*pH*
Cd	1.000	0.425*	-0.268 ^{ns}	-0.062 ^{ns}	0.116 ^{ns}	0.027 ^{ns}	0.480*	0.473*	0.445*	0.408*	0.224 ^{ns}	0.350 ^{ns}
Cu		1.000	-0.127 ^{ns}	-0.043 ^{ns}	0.167 ^{ns}	0.296 ^{ns}	-0.009 ^{ns}	0.341 ^{ns}	0.409*	0.350 ^{ns}	-0.081 ^{ns}	0.276 ^{ns}
Fe			1.000	-0.459*	-0.312 ^{ns}	0.329 ^{ns}	-0.338 ^{ns}	-0.309 ^{ns}	-0.484*	-0.464*	-0.415*	-0.443*
Ni				1.000	-0.271 ^{ns}	-0.153 ^{ns}	-0.004 ^{ns}	0.461*	0.334 ^{ns}	0.406*	0.289 ^{ns}	-0.059 ^{ns}
Pb					1.000	-0.157 ^{ns}	0.248 ^{ns}	0.189 ^{ns}	0.290 ^{ns}	0.314 ^{ns}	-0.054 ^{ns}	0.418*
Zn						1.000	-0.044 ^{ns}	0.122 ^{ns}	0.040 ^{ns}	-0.001 ^{ns}	0.221 ^{ns}	-0.164 ^{ns}
Temp							1.000	0.249 ^{ns}	0.276 ^{ns}	0.276 ^{ns}	0.192 ^{ns}	0.217 ^{ns}
Cond								1.000	0.849***	0.893***	0.362 ^{ns}	0.242 ^{ns}
TDS									1.000	0.956***	0.222 ^{ns}	0.337 ^{ns}
Sal										1.000	0.217 ^{ns}	0.369 ^{ns}
DO											1.000	-0.004 ^{ns}
pH												1.000

Note: All parameters were $\log_{10}$ (mean+1) transformed prior to correlation analysis. Values given are the correlation coefficients (r) and their levels of significance (^{ns}P >0.05, $^{*}P$ <0.05, $^{**}P$ <0.01, $^{***}P$ <0.001).

Table 3: Multiple linear stepwise regression analysis of dependent variables (dissolved metals based on their $\log_{10}$ transformed concentrations) in the rivers and drainage waters. The coefficient of correlation, r2, for all equations are 0.99 (N = 24).

Dissolved metals	*a*	*b_1*	*b_2*	*b_3*	*b_4*	*b_5*	*R2*	*F*	*P*
Cd	-0.098	Temp 0.069	Sal 0.011	-	-	-	0.56	13.43	0.0002
Cu	*								
Fe	0.366	Ni -2.63	Zn 4.62	DO -0.305			0.67	13.51	0.0001
Ni	0.024	Cd -1.62	Fe -0.037	Pb -0.082	Cond 0.016	-	0.56	6.09	0.0025
Pb	-0.497 0.69	pH	-	-	-	-	0.15	3.94	0.0598
Zn	0.006	Fe 0.108	-	-	-	-	0.55	27.16	0.0001

Note: Independent variables included Temp = temperature, Cond = conductivity, TDS = total dissolved solids, Sal = salinity, DO = dissolved oxygen, pH and dissolved metals.
* indicated no variable met the 0.15 significance level for entry in the model.

only weakly correlated with pH (R = 0.42). When the relationship is based on SRA, dissolved Cd is also only influenced by pH. Interestingly, dissolved Zn did not significantly correlate with any of the physico-chemical parameters and dissolved metals. When the relationship is based on SRA, dissolved Zn is significantly influenced by dissolved Fe.

This indicated that most of the dissolved metals are hardly influenced directly by the measured physico-chemical parameters during the time of sampling. This may indicate that measurement of using dissolved metals in the water samples are almost independent of the physico-chemical variations of those measured in this study. This could be due to the fact that other chemical characteristics, which are not measured in this study, can directly influence availability and dissolved concentrations of dissolved heavy metal concentrations.

Although there is some argument that water samples do not necessary reflect the pollution levels of the sampling sites since the water chemistry and water quality changes from time to time (Seng et al., 2003), the data based on water quality should be an indicator of the water quality at the time of sampling. However, regardless of the high variation of the water quality, the results obtained can be still representative of the spatial variation of the water quality throughout a wide geographical area from Kuala Perlis to southern Johore.

Conclusion

The wide range of dissolved metal concentrations especially at a few sites together with poor water quality indicated the anthropogenic inputs into the drainages and rivers. Although it is impossible to determine the negative impacts of the high dissolved concentrations of heavy metals and the poor water quality to the living biota, the present data signified the anthropogenic inputs. Therefore, it is important to mitigate and control the illegal discharges of wastes by the industries and urban communities. Perhaps, 'love our rivers' campaign that was previously launched in Malaysia some years ago should be relaunched. Regular monitoring of water quality in all drainage waters is recommended.

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