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Multivariate analysis of heavy metals concentrations in river estuary

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Abstract Multivariate statistical techniques such as multivariate analysis of variance (MANOVA) and discriminant analysis (DA) were applied for analyzing the data obtained from two rivers in the Penang State of Malaysia for the concentration of heavy metal ions (As, Cr, Cd, Zn, Cu, Pb, and Hg) using a flame atomic absorption spectrometry (F-AAS) for Cr, Cd, Zn, Cu, Pb, As and cold vapor atomic absorption spectrometry (CV-AAS) for Hg. The two locations of interest with 20 sampling points of each location were Kuala Juru (Juru River) and Bukit Tambun (Jejawi River). MANOVA showed a strong significant difference between the two rivers in terms of heavy metal concentrations in water samples. DA gave the best result to identify the relative contribution for all parameters in discriminating (distinguishing) the two rivers. It provided an important data reduction as it used four parameters (Zn, Pb, Cd and Cr) affording 100% correct assignations. Results indicated that the two rivers were different in terms of heavy metals concentrations in water, and the major difference was due to the contribution of Zn. A negative correlation was found between discriminate functions (DF) and Cr and As, whereas positive correlation was exhibited with other heavy metals. Therefore, DA allowed a reduction in the dimensionality of the data set, delineating a few indicator parameters responsible for large variations in heavy metal concentrations. Correlation matrix between the parameters exhibited a strong evidence of mutual dependence of these metals.

Keywords River estuary · MANOVA · Discriminant analysis · Heavy metal · F-AAS · CV-AAS

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Introduction

Malaysia is presently undergoing rapid industrial development and there have been incidences of toxic pollution from industry. Solid and liquid wastes emanating from the industrial activities are the inevitable by products of manufacturing process. A number of natural and anthropogenic sources produce heavy metals and people are becoming more aware of the complexity of the nature and the delicate balance that exist within the global ecosystem (Ahmet et al. 2006). Most of the degradation of rivers worldwide and their estuaries water quality is due to anthropogenic impacts from the surrounding areas close to their locations. Heavy metals are among the most common environmental pollutants and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources (Singh et al. 2005). In contrast with organic pollutants, heavy metals cannot be biologically or chemically degraded at all, and thus may either accumulate locally or be transported over long distances (Guo et al. 1997). The main natural sources of metals into the aquatic system are the weathering of soils and rocks and from anthropogenic activities, whereby industrial and urban wastes are discharged into water bodies (Pardo et al. 1990; Boughriet et al. 1992; Klavins et al. 2000; Yu et al. 2001). Department of Environment (DOE 1995) of Malaysia has reported higher concentrations of heavy metals in the waters of the north-west coast of Peninsular Malaysia compared to other areas because of the extensive land use and industrialization.

The application of multivariate methods has increased tremendously in recent years for analyzing environmental data (Tuncer et al. 1993; Einax and Soldt 1999; Abd-wahab et al. 2005). Multivariate methods are useful where several dependant variables are mea-

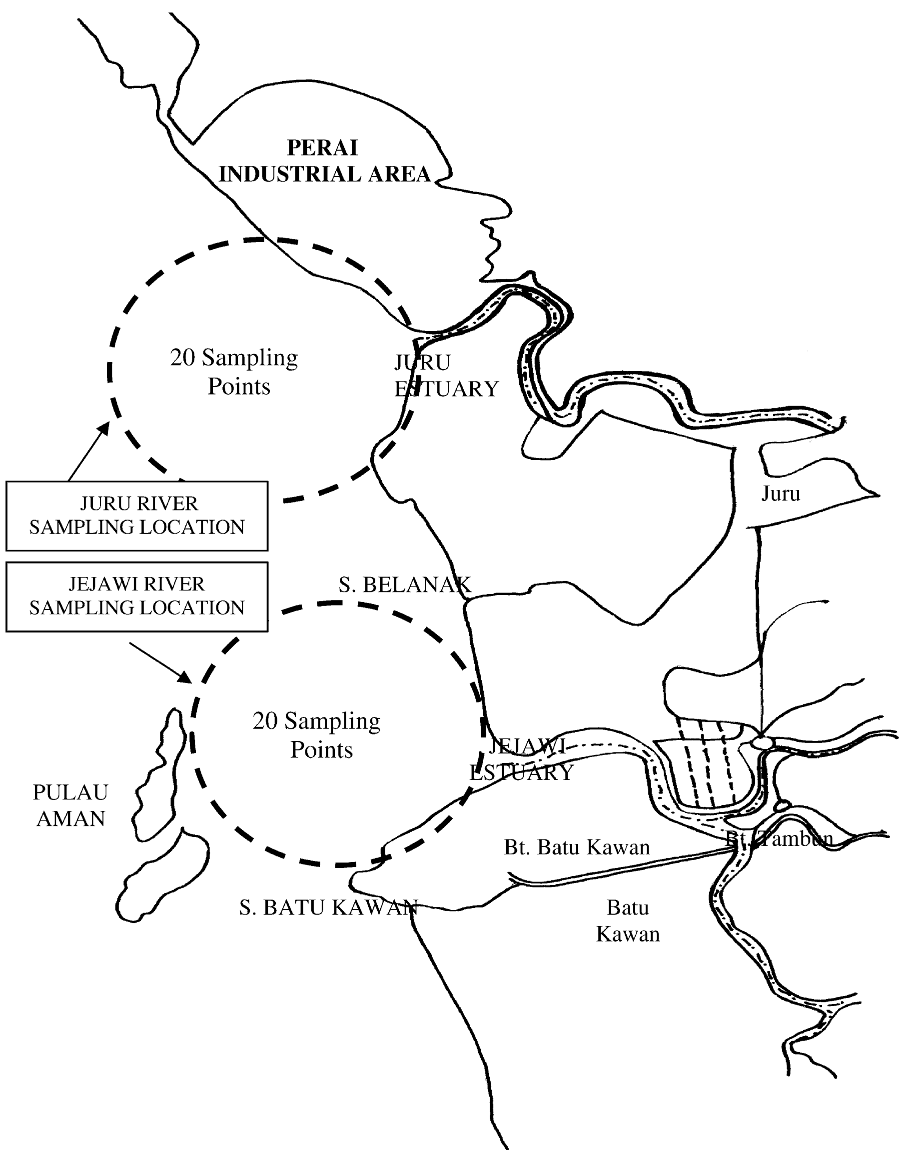

Fig. 1 Map of sampling locations for study areas

sured on each sampling unit. Multivariate analysis of variance (MANOVA) has been used to test the significant differences, while discriminant function (DF) has been used to identify the relative contribution of all variables to the separation of the groups (Richard and Dean 2002; Alvin 2002).

The objective of this study was to determine, on the basis of concentrations of seven metal ions (Cu, Pb, Cd, Cr, As, Zn, and Hg), whether the source of these heavy metals in water sampled from two different rivers are different. In addition it is important to identify the relative contribution of all parameters for distinguishing the two rivers according to the contribution of above selected parameters.

The present paper describes the use of multivariate statistical technique for identifying the relative contribution of all metals ions in the rivers Juru and Jejawi as well as to assess the over all quality of water.

Materials and methods

Description of study area

The study site is located on the North West coast of peninsular Malaysia, in the state of Penang and within a coastal mudflat in the Juru and Bukit Tambun district (Fig. 1). The sites are located adjacent to industrial areas which were reclaimed from mangrove. The types of industry presently in operation include electronics, textiles; basic and fabricated metal products, food processing and canning, processing of agricultural products, feed mills, chemical plants, rubber based industry, timber based wood products, paper products and printing works, and transport equipment. Other main activities that are operating in vicinity of this area are ships' harbour with petroleum unloading and a red earth quarry which extends right up to the coastline. There are three main rivers flowing into the area, Sungai Juru, Sungai Semilang and Sungai Jejawi where some fishing villages are situated.

Table 1 Descriptive statistics of heavy metals concentrations in water obtained from Juru River (mg/l)

Metal	Minimum	Maximum	Mean	SD
Cu	0.00	0.18	0.05	0.04
Pb	0.13	0.47	0.31	0.08
Zn	0.06	0.11	0.09	0.02
Cd	0.12	0.28	0.17	0.05
Cr	0.03	0.15	0.12	0.04
As	1.67	5.98	3.38	1.01
Hg	0.01	0.04	0.02	0.01

Table 2 Descriptive statistics of heavy metals concentrations in water obtained from Jejawi River (mg/l)

Metal	Minimum	Maximum	Mean	SD
Cu	0.01	0.06	0.05	0.01
Pb	0.15	0.39	0.25	0.06
Zn	0.04	0.08	0.05	0.01
Cd	0.05	0.28	0.14	0.05
Cr	0.12	0.28	0.20	0.04
As	2.83	3.84	3.44	0.29
Hg	0.00	0.02	0.01	0.00

Water sampling and analyses

Five water samples were collected from each of 40 estuarine sites in Juru and Jejawi Rivers (20 sites from each estuary) during a rainy season in the year 2005 as showed in Fig. 1. All water samples were kept in polyethylene bottles (previously washed with detergent, then with deionized water, 2 M nitric acid, and then deionized water again). Finally, samples were acidified with 10% HNO_3, placed in an ice box and then brought back to the laboratory for analysis.

The samples were filtered through Whatman filter paper number 1 and preserved at 4°C in the low temperature refrigerator. For the analysis purposes the preserved sample was taken out from the refrigerator and kept at room temperature until the attainment of thermal equilibrium. Prior to AAS analysis, a volume of 100 ml-filtered samples was digested with concentrated HNO_3 on a water bath (model Memmert) for 30 min until the sample volume is reduced to 30 ml. All samples were analyzed according to American Public Health Association Standard Method for Water and Wastewater Analysis (APHA 1999). Then the total metal ion concentrations of lead (Pb), zinc (Zn), chromium (Cr), mercury (Hg), copper (Cu), arsenic (As) and cadmium (Cd) in the filtered and digested samples were determined by flame AAS (FAAS) except Cd which was analyzed through cold-vapour (CV) AAS method (Perkin Elmer Model Analyst 100, USA). The data quality was checked by careful standardization, procedural blank measurements, spiked and triplicate samples.

Table 3 Mean concentrations heavy metals in water obtained from Juru and Jejawi Rivers with comparison to Malaysian Standard

Metals	Mean concentration of metals studied			Malaysia standard	
	Juru (mg/l)	Jejawi (mg/l)	INWQS; class II[a] (mg/l)	EQA 1974 (mg/L)	
				StandardA (mg/l)	Standard B (mg/l)
Cu	0.05	0.05	0.01	0.1	0.5
Pb	0.31	0.25	0.02	0.05	0.1
Zn	0.09	0.05	–	0.1	0.5
Cd	0.17	0.14	0.01	0.01	0.02
Cr	0.12	0.20	0.05	Cr^{3+}; 0.2 Cr^{6+}; 0.05	Cr^{3+}; 1.0 Cr^{6+}; 0.05
As	3.38	3.44	0.05	0.05	0.1
Hg	0.02	0.01	0.001	0.01	0.05

[a] Water supply with conventional treatment required.

Fishery – protection of sensitive aquatic species

Recreational use with body Contac

Statistical analysis

Multivariate analysis of variance (MANOVA)

Multivariate analysis of variance is used where several dependent variables (p) are measured on each sampling unit instead of one variable. The objective of MANOVA is to compare the mean vectors of $\boldsymbol{k}$ groups for significant difference. Equality of the mean vectors implies that the $\boldsymbol{k}$ means are equal for each variable, and if two means differ for just one variable then we conclude that the mean vectors of the $\boldsymbol{k}$ groups are different.

Discriminant analysis

Discriminant analysis is a multivariate technique used for two purposes:

(a) Descriptionof group separation—The linear functions of the several variables of discriminant functions (DFs) are used to elucidate the differences between two or more groups and identifying the relative contribution of all variables in the separation of the groups

(b) Prediction or allocation of observations to group—The linear or quadratic functions of the variable of classification functions (CFs) are used to assign an observation to one of the groups (Richard and Dean 2002; Alvin 2002).

Result and discussion

Descriptive statistics

Descriptive statistics for Juru and Jejawi Rivers including the mean, maximum, minimum values and standard deviation are reported in Table 1 and Table 2, The mean values of metal concentrations was arranged in the order; As>Pb>Cd>Cr>Zn>Cu>Hg, and As>Pb>Cr>Cd>Zn>Cu> Hg for Juru and Jejawi Rivers, respectively. Therefore, the concentrations of As and Pb exhibited higher levels in water, whereas those of Cu and Hg exhibited the lowest. In fact, the maximum values of As and Pb concentrations from Juru River

Table 4 Linear correlation coefficient matrix for heavy metals in Juru River

Metal	Cu	Pb	Zn	Cd	Cr	As	Hg
Cu	1						
Pb	−0.19	1					
Zn	0.19	−0.53*	1				
Cd	−0.44	−0.22	0.01	1			
Cr	−0.45*	−0.29	−0.34	0.56*	1		
As	0.40	−0.21	0.17	−0.01	0.13	1	
Hg	0.18	0.31	−0.06	−0.47*	−0.60**	−0.25	1

*Correlation is significant at the 0.05 level.; **Correlation is significant at the 0.01 level.

Table 5 Linear Correlation coefficient matrix for heavy metals Jejawi River

Metal	Cu	Pb	Zn	Cd	Cr	As	Hg
Cu	1						
Pb	0.32	1					
Zn	0.01	0.33	1				
Cd	−0.55*	−0.23	0.02	1			
Cr	0.23	−0.24	−0.13	−0.62**	1		
As	−0.01	0.24	0.31	0.50	−0.46*	1	
Hg	−0.10	−0.05	0.14	0.26	−0.06	−0.05	1

*Correlation is significant at the 0.05 level.; **Correlation is significant at the 0.01 level

were 5.98 mg/l and 0.47 mg/l, respectively, whilst the minimum values of Cu and Hg were 0.0 mg/l and 0.01 mg/l, respectively. The maximum values of As and Pb concentrations from Jejawi River were 3.84 mg/l and 0.39 mg/l, respectively, whilst the minimum values of Cu and Hg were 0.01 mg/l and 0.0 mg/l, respectively. Cd and Cr have interchanged their concentration ranking in water sampling in the two rivers.

In general, the observed spread around mean metal concentration was substantially low and random. However, Hg showed the lowest concentration in water samples from both rivers. Further, the reported mean concentration of heavy metals in water is given in Table 3 with comparison to Interim National Water Quality Standard (INQWS; DOE 2000) and Environmental Quality Act (EQA) 1974 Regulations 1979 for Malaysia (DOE 2000).

The mean concentration of As in water was 3.38 mg/l for Juru River and 3.44 mg/l for Jejawi River. Furthermore, the mean concentration of Pb in water was 0.31 mg/l for Juru River and 0.25 for Jejawi River, while the mean concentration of Cd was 0.17 mg/l for Juru River and 0.14 mg/l for Jejawi River. These values were higher than the permissible limit established by Interim National Water Quality Standard (INQWS) and Environmental Quality Act (EQA) and Regulations 1979 for Malaysia. The mean concentrations of Cu, Zn, Cr, and Hg for both rivers were lower than the permissible limit (INQWS and EQA). The mean concentrations of Cu in water for both rivers are similar (0.05 mg/l).

Table 6 Multivariate test (MANOVA) for both locations

Test	Value	F	*p* value
Pillai's Trace	0.79	16.65	<0.01
Wilks' Lambda	0.22	16.65	<0.01
Hotelling's Trace	0.36	16.65	<0.01
Roy's Largest Root	0.36	16.65	<0.01

Table 7 Wilks' Lambda for testing discriminant function validity

Test of Function(S)	Wilks' Lambda	Chi-square	*p* value
1	0.22	52.97	<0.01

The two rivers are considered as polluted drinking water sources with As, Pb, and Cd. It may also be an indicator of untreated and partially treated effluent discharged from nearby industrial area due to EQA 1974 (EQA 1974 2001) noncompliance. According to report by DANCED (DANCED 1998) the electroplating, pulp and paper, textiles, food and beverages and auto-workshops industries were closely linked to industrial pollution in the Prai industrial area. This in line with the report conducted by department of environment (DOE 1999) that the predominant polluting industries of Penang are electronic/electrical, textiles, fabricated metal products, plastic and plastic products. Other industries include rubber based, paper and paper products/printing works, chemical/fertilizers and basic industries.

The correlations of heavy metals concentrations in water samples from the two rivers were examined and the relevant data for Juru and Jejawi Rivers are given in Tables 4 and 5, respectively. For Juru River a strong negative relationship was exhibited between Hg and Cr, while Cr positively correlated with Cd and negatively with Cu. This indicates that Cr in water samples has a strong association with other metal and it shares a common origin with them. Negative relationship was exhibited between Zn and Pb. Hg was negatively correlated with Cd. For Jejawi River, a strong

Table 8 Correlation coefficients between all metals and discriminant function

Metal	Correlation
Zn	0.77
Cr	−0.65
Hg	0.33
Pb	0.23
Cd	0.18
Cu	0.03
As	−0.02

Table 9 Classification results for discriminant analysis of the two rivers

Locations	Percent correct	Predicted group membership	
		1	2
Juru River	100	20	0
Jejawi	100	0	20

100.0% of original grouped cases correctly classified.

negative relationship was exhibited between Cr and Cd and As. While negative relationship was exhibited between Cd and Cu. In summary, it can be said that, the results of the correlation exhibit a strong evidence of mutual dependence of these heavy metals.

Multivariate analysis

The results of multivariate analysis of variance (MANOVA) for metal concentrations are presented in Table 6. According to these results, the concentrations of heavy metals from the two rivers exhibit strong significant difference in terms of concentrations of selected heavy metals. Spatial variations in heavy metal concentrations were further evaluated through DA. Discriminant analysis was carried out to the data consisted of seven parameters. Only one discriminant function was found to discriminate the two rivers as shown in Eq. 1. Wilk's Lamda test showed that DF is statistically significant as shown by $p<0.01$ in Table 7. Furthermore 100% of the total variation between the two rivers was explained by one DF. The relative contribution for each parameter is given in Eq. 1

$$Z = -0.01\ \mathrm{Cu} + 0.36\ \mathrm{Pb} + 0.81\ \mathrm{Zn} + 0.29\ \mathrm{Cd} - 0.25\ \mathrm{Cr} - 0.076\ \mathrm{As} + 0.21\ \mathrm{Hg} \quad (1)$$

Zinc exhibited high contribution in discriminating the two rivers and account for most of the expected variations in metal concentrations, while other parameters showed less contribution in explaining the variation between the two rivers.

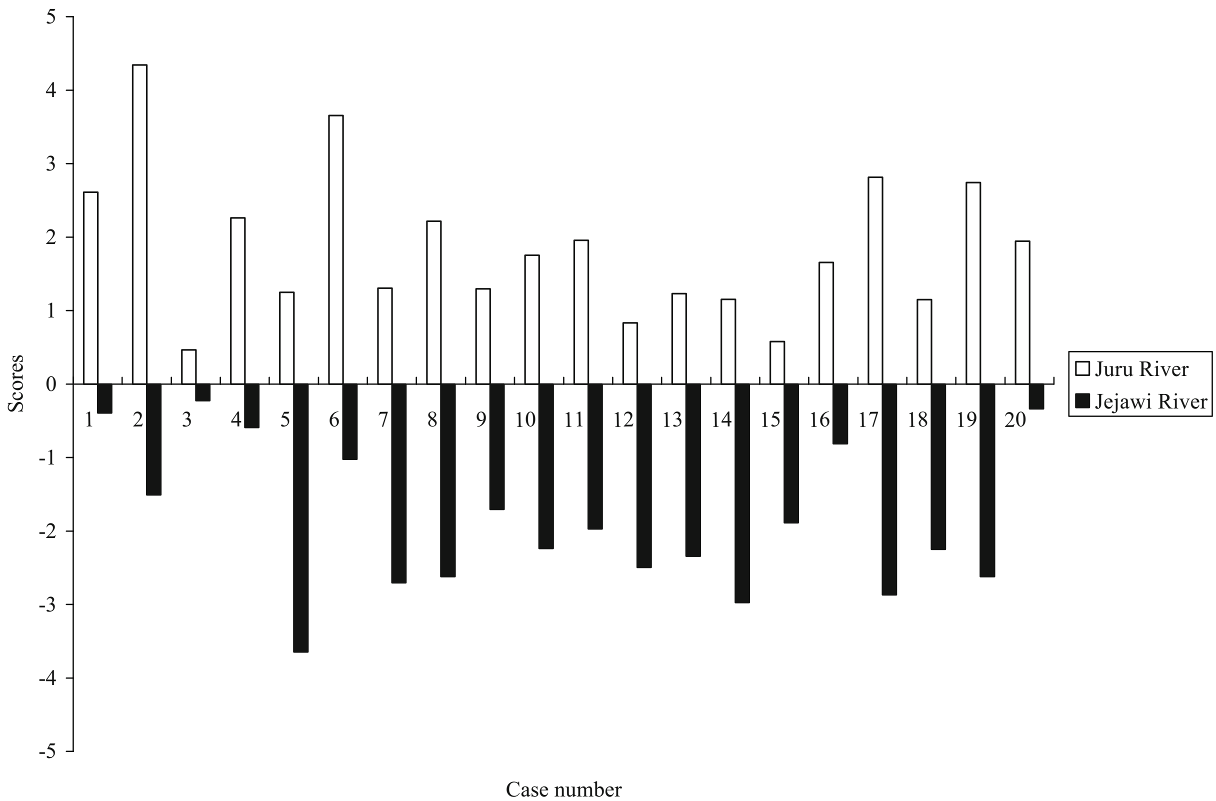

Fig. 2 Scores for the standardized discriminant function

The relative contribution for all metal concentrations can be arranged in the order; Zn>Pb>Cd>Cr>Hg>As>Cu.

Correlation data between metal concentrations and DF are summarized in Table 8. Both Zn and Cr were seen to be strongly correlated with Eq. 1 where as Cu and As were not strongly correlated. The classification matrix (Table 9) showed that 100% of the cases were correctly classified to their respective groups. The result of classification showed that significant differences exhibited between the two rivers, which are expressed in terms of one discriminant function.

Relationship between sampling points

An attempt was also made to study the relationship between the scores of discriminant function and the samples from various locations (Fig. 2) that corresponds to the scores of discriminant function for various samples. The samples numbers 1–20 corresponds to water samples along 20 sampling points of each river. It could be seen from Fig. 2 that all points of Juru River showed positive contribution to discriminant function, whereas all points of Jejawi River showed negative contribution. This could be due to differences in industrial and agricultural activities operating close to the study areas such as rubber manufacturing, pulp, paper, electroplating and metal finishing industrial sector. According to Mahajan (1985) electroplating and metal-finishing industries produce liquid waste containing metallic ions such as zinc, copper, lead, nickel, chromium, silver, cadmium, mercury which are toxic to the flora and fauna and inhibit the self-purifying processes of the water bodies when the concentration discharge is higher than the permissible limit. In summary, the heavy metal concentrations of Zn, Pb, Cd, and Hg were higher in water samples obtained from Juru than Jejawi River.

Conclusions

The application of multivariate statistical technique has been proved to be an effective tool for identifying the relative contribution of all metals. It may also be concluded that the heavy metal concentrations in water obtained from Juru and Jejawi Rivers are different based on MANOVA result. It was also observed that Zn was responsible for large variations in the data according to its coefficient with DF, furthermore, only four parameters (Zn, Pb, Cd, and Cr) affording 100% correct assignations. Thus, DA gave an interesting result in evaluating and understanding the source of spatial variations.

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