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SPATIAL DISTRIBUTION OF PHYSICO-CHEMICAL PARAMETER IN UPSTREAM RIVERS AND TIMAH TASOH LAKE, PERLIS: PRELIMINARY STUDY

(Taburan Spatial Parameter Fizikal-Kimia Di Sungai Dan Empangan Timah Tasoh, Perlis: Kajian Permulaan)

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Abstract

Rivers located in the northern part of Perlis which are used as a source of fresh water for Tasoh Dam are exposed to heavy metals pollution since all industrial and agricultural waste were directly discharged into rivers. In order to determine the distribution pattern of heavy metals in rivers and dam, the physico-chemical parameter forms of metals were investigated. Surface water sample were collected randomly from selected sampling site and were analysed for lead (Pb), copper (Cu), chromium (Cr), arsenic (As) and manganese (Mn) using Inductive Coupled Plasma Mass Spectrometry (ICP-MS). The concentration range of the metals were; 0.37-2.37 ppb, 0.23-3.27 ppb, 0.57-6.8 ppb, 0.27-12.60 ppb and 7.00-383.83 ppb respectively. All measured metals were found to be below the permissible limit set by Department of Environment Malaysia except for manganese. The sources of Mn were come from industrial activities such as textiles, chemical, food industry which directly discharged waste water into river.

Keywords: heavy metals, pollution,distribution, spatial,anthropogenic

Abstrak

Sungai yang terletak di bahagian utara Perlis yang digunakan sebagai sumber air tawar untuk Empangan Tasoh terdedah kepada pencemaran logam berat kerana semua sisa industri dan pertanian terus dilepaskan ke dalam sungai. Untuk menentukan corak taburan logam berat dalam sungai dan empangan, parameter fiziko-kimia logam telah dikaji. Sampel air dipermukaan telah diambil secara rawak dari kawasan pensampelan yang dipilih dan dianalisis bagi plumbum (Pb), kuprum (Cu), kromium (Cr), arsenik (As) dan mangan (Mn) menggunakan *Inductively Coupled Plasma-Mass Spectrometry* (ICP-MS). Julat kepekatan logam; 0,37-2,37 ppb, 0,23-3,27 ppb,,57-6,8 ppb,,27-12,60 ppb dan 7,00-383,83 ppb masing-masing. Semua logam yang diukur didapati berada di bawah had yang dibenarkan oleh Jabatan Alam Sekitar Malaysia kecuali mangan. Sumber-sumber bagi Mn datang daripada aktiviti industri seperti tekstil, kimia, industri makanan yang terus dilepaskan sisa ke dalam sungai.

Kata kunci: logam berat, pencemaran, taburan,spatial,antropogenik

Introduction

Water is the most vital resources in all aspects of human, ecosystem, survival and health. However with the rapid growth in urbanization and industrialization, water can be easily contaminated [1]. Among of various pollutants exist on earth, heavy metals are the most toxic pollutants present in surface waters, tend to accumulate in organisms and become persistent due to their chemical stability and readily soluble [2]. Those metals are environmentally mobile and may enter human food chain which in turn give a harmful effect to human and living things [3].The most toxic metals are Cr, Ni, Pb, Cd and As while metals such as Mn, Co, Cu, and Zn act as the essential micronutrients for flora and fauna, but they are still dangerous at high levels. In addition, environmental factor such as temperature, pH dissolved oxygen, salinity can influence the toxicity of metals in solution [2].These metals enter and distributed into water bodies by weathering and erosion or anthropogenic activities such as industrial processing, agricultural runoff and sewage disposal [4].

Timah Tasoh Dam located in Northern part of Perlis is the major source of drinking water, industrial, agricultural and also used for irrigation and flood control [5]. Rivers that supply freshwater into the Dam are Pelarit and Jarum Rivers. The influence of human activities in the upstream until downstream catchments area of both rivers such as agriculture, housing, recreation contributes to the degradation of water quality of the lake [5].These activities resulting in large scale deterioration of the water quality in dam. To date, there have been no systematic studies on this river in upstream and downstream as well as in dam although well planned monitoring programmed has been conducted by Department of Environment [6]. Therefore, it is important to investigate the spatial distribution of physico-chemical parameter in order to control the water quality of upstream rivers and dam, since they are mainly use for drinking, industrial and agricultural purpose. The objective of this study was to investigate the spatial distribution of physico-chemical parameter in Upstreams Rivers and Timah Tasoh Lake.

Materials and Methods

Description Of Study Area

TimahTasoh Lake, Perlis (6^o 36^oN and 100^o 14'E) located approximately 13 km north of the Kangar town near the Thailand boarder. The average surface area is about 13.33 km^2 and able to store capacity up to 40 million meter cube.Two main river which are Jarum (64.4 km^2) and Pelarit River (42[illegible] km^2) are the most important sources of freshwater for dam where the upstream of these river is located at Perlis State Park (st4) and Post Razi(st 1) as showed in figure 1 [5]. Water from upstream will flow through another six rivers namely Rimba Mas (st 2), Jarum River (st 3), Wang Kelian River (st 5), Gua Kelam (st 6), Gua Wang Mo (st 7), Wang Mo River (st 8), Pelarit River (st 9) and lastly its enter Tasoh Lake (st 10). Based on the observation, there was an agricultural area in upstream catchments such as rubber, paddy, sugar, cane, timber plantation and livestock surrounding Dam [5]. Those activities were identified as non-point source pollution. Meanwhile domestic and industrial zone was categorized as point source pollution to the Tasoh Lake [5.] Both sources of pollutions may contribute to the depletion of water quality. Figure 1 below illustrates the location of sampling site.

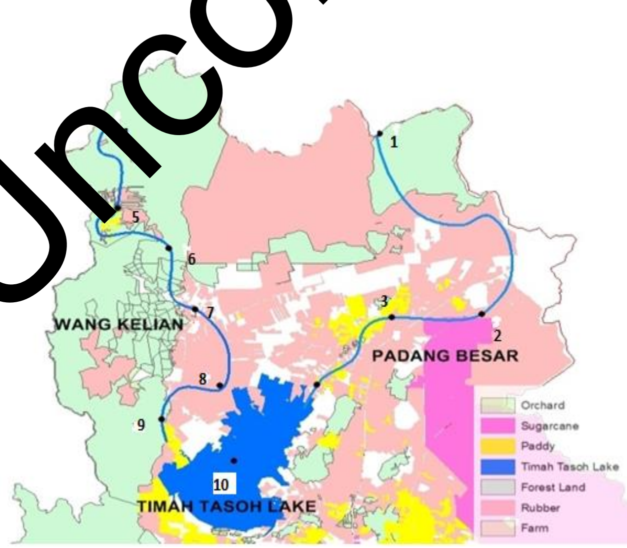

Figure 1: Location map for sampling site

Sampling and pre-treatment

About 30 surface samples were collected using Niskin water sampler from 10 sampling points with the help of Global Positioning System (GPS Map 76Cx) on May and June 2012 during dry season. Water sample was kept in 500ml polyethylene sample bottle and was acidified with concentrated HNO_3 to pH <2. All preserved water samples were kept in coleman box using ice cubes and transported to the Green Environmental Research Laboratory at Unversiti Teknologi MARA Arau, Perlis. All preserved samples were transferred into incubator at 4^oC before used in analysis. Six of *in-situ* parameter such as temperature, salinity, dissolves oxygen, conductivity, pH and total dissolved solid were measured directly at each station using HYDROLAB DataSonde

Water Analysis

All preserved water samples were filtered through pre-washed 0.45 µm Milipore nitrocellulose filters and the initial portion of the filtration was discarded to clean the membrane. 1 mL filtered samples was then transferred into a pre-cleaned centrifuge tube and adjusted with deionised water from Mili-Q water system to 10 mL. Samples were then ready to be analyzed with ICP-MS. Mili-Q water system and analytical grade reagents were used throughout the work. Standard Reference Material 1643e (SRM) for fresh water and reagent blank were used for quality control sample during analysis. The percent recovery of metals is acceptable which is within 80-120%. The standard solution used for calibration was prepared by diluting stock solution of 1000 mg/L of multi element standards.

Results and Discussion

Table 1 revealed that the temperature was varied from 24.0-33.6 ^oC; mainly because of different timing during sampling as well as the effect of atmospheric temperature [7]. The TDS values of the study area lies between 0.033 – 0.452 g/L. This varied value was due to the increase of various kinds of minerals such as ammonia, nitrite and metallic ion which comprised of dissolved solid in water [8]. The lowest value of salinity observed was 0.02% meanwhile the highest value is 0.34%. The possible reason salinity give varied values is because of the presence of ionic substance that come from the reaction occur between metals and acid in water [8]. The range of DO obtained was from 9.93 -16.48 mg/L. High value of DO at Station 3 located at Jarum River possibly to the increase of temperature during dry season lead to acceleration of the photosynthesis which utilizing carbon dioxide and giving off oxygen [9]. The pH value varied from 7.0 – 8.5 which is within the permissible limit for diverse uses such as water supply, fishery set by DOE (pH 6.5-8.5). The electrical conductivity (EC) obtained is in the range from 0.051-0.395 mS/cm. The highest values of EC were found at Station 3. This may come from the addition of waste water from residential area near the river as well as from industrial activities such as textile, chemical and rubber made industries which are located at Padang Besar Town [10]. Beside that, EC may naturally come from the origin of the river water and due to inert stream bank material [10].

In term of spatial distribution pattern of heavy metals, overall result show all reading give the same graph pattern between May and June samples (as shown in Figures 2(a)-2(e). However, the level of heavy metal's concentration of in this two months is different. This may caused by a prolonged summer occurred causing the water to recede and shallow. When depth, temperature and river flow change, it will result in changes of the equilibration between sediment and water. This will result in the oxidation of solid metals compounds and resuspension of sediments would release entrapped soluble metals in sediment into the water [11].

However, this pattern was occur due to the influence of anthropogenic activities for example in Fish Temple at Station 7 there was an illegal dumping wastes which accumulated at the end of the stream. Diesel and plaster ceiling factories found in Station 2 located at Padang Besar also give significant bad impact and contamination to the river. But the major sources of pollutant in Jarum River (Station 3) is due to the existing of residential area that generate solid waste and sewage which were directly discharge into the river [5].

Table 1: Mean value for physical parameter in May and June*

Sampling station	Location	Mean value for physical parameter in May (June)					
		T (^oC)	**TDS (g/L)**	**Salinity (%)**	**DO (mg/L)**	**pH**	**EC (mS/cm)**
1	N 6^0 41.411’ E 100^O 16.853’	26.67 (27.3)	0.4333 (0.452)	0.32 (0.34)	13.00 (12.03)	7.3 (7.3)	0.360 (0.353)
2	N 6^0 38.213’ E 100^0 17.531’	29.57 (30.4)	0.229 (0.129)	0.17 (0.17)	10.21 (12.71)	7.3 (7.4)	0.384 (0.214)
3	N 6^0 36.843’ E 100^0 14.697’	28.83 (33.6)	0.239 (0.286)	0.17 (0.21)	11.15 (16.48)	7.0 (7.9)	0.395 (0.395)
4	N 6^0 41.052’ E 100^O 11.334’	24.6 (24.9)	0.033 (0.034)	0.02 (0.02)	15.68 (16.16)	7.1 (7.6)	0.051 (0.052)
5	N6^o 39.511’ E100^O 11.026’	26.74 (27.8)	0.194 (0.221)	0.14 (0.16)	14.17 (13.25)	7.2 (7.7)	0.308 (0.359)
6	N 6^0 38.746’ E 100^0 12.023’	26.55 (26.50)	0.236 (0.236)	0.17 (0.17)	14.81 (14.81)	7.5 ([illegible].5)	0.374 (0.374)
7	N6^0 38.746’ E 100^0 12.366’	26.43 (26.5)	0.227 (0.237)	0.17 (0.17)	[illegible] (13.[illegible]4)	7.7 (8.1)	0.359 (0.375)
8	N6^0 36.811’ E 100^0 12.251’	26.62 (26.3)	0.223 (0.245)	0.17 (0.18)	1[illegible].42 (14.55)	7.6 (7.7)	0.327 (0.387)
9	N6^0 35. 512’ E 100^0 12.432	27.21 (27.1)	0.224 (0.238)	0.1[illegible] (0.[illegible]7)	12.77 (12.59)	7.0 (8.0)	0.361 (0.375)
10	N 6^{O}34.509’ E 100^0 12.237’	30.18 (29.20)	0.218 (0.145)	[illegible]09 (0.1[illegible])	13.58 (12.37)	7.6 (8.6)	0.217 (0.209)

*in bracket is refer to value in June

Table 2: Concentration of metals in surface water in ppb unit

Sampling station	Actual Concentrations in ppb May and June*				
	Pb	**Cd**	**Cr**	**As**	**Mn**
1	0.43 (0.60)	0.23 (0.30)	3.63 (6.87)	0.27(0.30)	26.77(31.83)
2	0.[illegible]0 (0.[illegible]7)	0.57 (1.07)	3.70 (4.67)	7.73(4.40)	383.83 (78.24)
3	0.90 (1.07)	0.57 (1.30)	3.33 (4.27)	2.07(2.90)	119.13(191.27)
4	1.4[illegible] (0.53)	0.43 (0.27)	0.60 (0.80)	7.07 (5.97)	43.63(11.37)
5	3.70 (0.17)	1.33 (0.23)	1.87 (0.57)	7.27(6.63)	165.50(121.90)
6	0.83 (0.73)	0.83 (1.50)	1.97 (1.27)	4.17(5.03)	67.80(94.97)
7	0.87 (0.57)	0.43 (0.50)	2.43 (3.93)	9.27(10.10)	7.00(39.83)
8	0.90 (0.73)	0.47 (0.93)	2.60 (3.30)	8.40(12.60)	46.27(66.80)
9	2.27 (2.00)	6.77 (2.07)	2.27 (1.37)	10.00(11.20)	91.17(105.50)
10	1.80 (1.30)	1.53 (2.07)	1.37 (0.97)	10.97(9.57)	132.03(128.43)
SRM Recovery (%)	110 (111)	100 (103)	110 (106)	84 (96)	94 (99)
INWQS (Class III)	14	12	2530	40	100

*in bracket is refer to value in June

The mean concentrations of metals in water are shown in Table 2. The range of metals during both month are Pb 0.37-2.37 ppb, As 0.27-12.60 ppb, Cu 0.23-3.27 ppb, Mn 7.00-383.83 and Cr 0.57-6.8 ppb, ppb respectively. As shown in Figure 2(a), the source of high concentration Pb in Station 5 on May was come from Hi-Clean Sewage Treatment Plant from nearest base camps which create wastewater into the stream [5]. Moreover, an illegal dumping waste directly into the river was found at this station.

The concentration of As in water ranged between 0.27-12.60 ppb as illustrated in Figure 2(b). The anthropogenic sources of high concentration of As at Station 8 is may come from wastewater discharged from factory producing mineral water and domestic wastes. However, As might occur naturally from the extensive evaporation of water due to high temperature and low rate of rain falls [12]. As in nonessential for plants but is an essential trace element in several animal species. Severe poisoning of As can arise from the ingestion of as little as 100 mg arsenic trioxide, chronic effects may result from the As compounds, in body at low intake levels. Carcinogenic properties also have been imputed to arsenic compounds depend on chemical forms [13].

The highest concentration of Cu in Station 9 as shown in Figure 2(c) is may come from the used Cu salts are in water supply system to controlled biological growth in reservoir and distribution pipes since this river is an important source of freshwater in Tasoh Dam [13]. Corrosion of copper that contain alloys in pipe fitting may introduce measureable amounts of Cu into water in pipe systems. Besides that, other possible sources of Cu is due to automobile activity such as the usage of copper in brake particles transportation in residential area [14].

Based on result in Table 2, the high level of Mn on May located at Station 2,3,5 and 10 as shown in Figure 2(d). Meanwhile on June, located at Station 3,5,9 and 10. River water at all of these stations were classified under Class III based on Interim National Water Quality Standard (INWQS) set by Department of Environment Malaysia due to the exceed limit of Mn in river water which is more than 100 ppb. The possible source of this highest concentration of Mn at Padang Besar area (Station 1-3) might come from industrial activities factories located at Padang Besar town such as textile, fiberglass, chemical, food and rubber made industry. The waste water from these industries was directly discharges into river [5]. There is no industrial activity reported at Wang Kelian area which is at Station 4-9 but extensive rubber and paddy cultivation as well as animal's livestock were reported at this area [5]. The used of fungicides and livestock feeding supplements in agricultural and livestock area may contain Mn compound could be the reason why Mn is exist in water bodies (WHO). Besides that, Mn may occur naturally in river since it's very essential for plants and animal growth but elevated Mn can give bad influence to those who consumed it [13].

Based on the Figure 2(e), highest concentration of Cr was found at Station 1 which is control area. This element can occur in natural water based on water hardness, the harder the water, the high level of Cr naturally exists in water. However, Cr is nonessential for plant but essential trace element for animals. Hexavalent of Cr such as CrO_4^{2-}, $Cr_2O_7^{2-}$ (absorbed by clay mineral) has been shown to be carcinogenic by inhalation and is corrosive to tissue [13]. In addition, based on INWQS the baseline value for Cr in water under Class III was 2530 ppb which is too high when compared with obtained result with the highest value was only 6.87 ppb recorded at Station 1.This can support that the existing Cr in water was come from natural sources.

The overall results obtained were compared with the Interim National Water Quality Standard for Malaysia set by DOE. The concentration of all metals remained below the permissible limit except for Mn which is above 100 ppb. These metal fall into Class III that is set by DOE which means an extensive treatment is required for the drinking water purposed as well as for fishery, livestock and drinking.

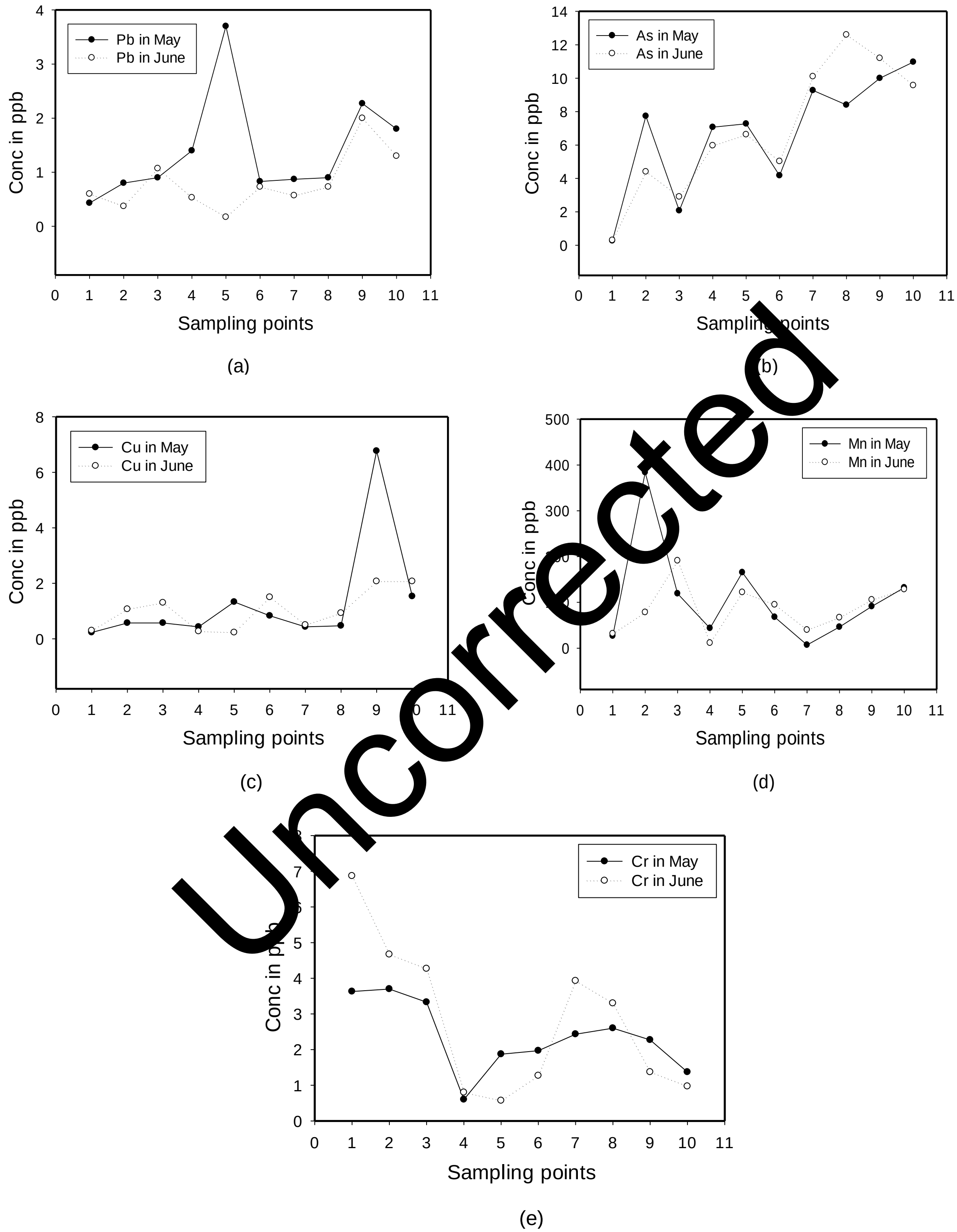

Figure 2: Distribution pattern of metals during May and June ; (a) lead , (b) arsenic, (c) copper, (d) manganese, (e) chromium

Conclusion

From the result, the preliminary study of distribution pattern of metals was varied through rivers and Lake. This indicates that there is unregulated discharge of contaminated effluent into water bodies without earlier treatment by responsible industries and communities within the study area. Results of this study provide baseline data which can be used for expanding this research. For the future work, statistical analysis and geographical information system (GIS) will be use in determination the sources of heavy metal contents in water within different areas as well as for modelling metals concentration distribution pattern in large scale area.

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References

1. Oyewale, A. O and Musa, I. (2006). Pollution assessment of the lower basin of Lakes Kainji/Jebba, Nigeria:heavy metal status of the waters, sediments and fishes. *Environ. Geochem. Health*, 28, 273-281.
2. Emoyam, O. O., Ogban, F. E., Akarah, E., (2006). Evaluation of Heavy Metals Loading of River Ijana in Ekpan – Warri, Nigeria. *J. Appl. Sci. Environ. Mgt. June,* 10 (2) 121 – 127.
3. Bhaskar, C. B., Kumar, K.., G. Nagendrappa. (2010) Assessment of Heavy Metals in Water Samples of Certain Locations Situated Around Tumkur, Karnataka, India.*E-Journal of Chemistry*, 7(2): 349 - 352
4. Kaushik, A., Kansal, A., Meena, A., Kumari, S., Kaushik, C. P. (2009). Heavy metal contamination of river Yamuna, Haryana, India: Assessment by Metal Enrichment Factor of the Sediments. *Journal of Hazardous Materials*, 164 265–270.
5. Kamarudzaman, A.N ., Feng, V. K.., Aziz, R. A., Jalil, M. F. (2011). Study of Point and Non Point Sources Pollution – A Case Study of Timah Tasoh Lake in Perlis, Malaysia. *International Conference on Environmental and Computer Science IPCBEE* ,19.
6. DOE., Malaysia Environmental Quality Report (2006). Department of Environmental Ministry of Science, Technology and Environment Malaysia.
7. Sharma , R., Capoor, A. (2010). Seasonal Variations in Physical, Chemical and Biological Parameters of Lake Water of Patna Bird Sanctuary in Relation to Fish Productivity. *World Applied Sciences Journal*, 8 (1): 129-132.
8. Lutfor, A. K. M., Islam, M., Hossain, M. Z., Ahsan, M. A. (2012). Study of the Seasonal Variations in Trag River Water Quality Parameters. *African Journal of Pure and Applied Chemistry*,. 6(10) : 144-148.
9. Lawson, E. O. (2011). Physico-Chemical Parameters and Heavy Metal Contents of Water from the Mangrove Swamps of Lagos Lagoon, Lagos, Nigeria. *Advances in Biological Research*, 5 (1): 08-21.
10. Eisakhani, M., Malakahmad, A.(2009). Water Quality Assessment of Bertam River and its Tributaries in Cameron Highlands, Malaysia.*World Applied Sciences Journal*, 7 (6) :769-776.
11. Chon, H. S., Ohandja, D., Nikolaos, V. (2012). The Role of Sediments as a source of metals in River Catchments.*Chemosphere* 88(10):1250-6.
12. Jameel, B. A., Tasneem, K. G., Muhammad A. B., Hassan, A. H. (2009). Evalutation of arsenic and other physic-chemical parameters of surface and ground water of Jamshoro, Pakistan.*Journal of Hazardous Materials*, 166, 662-669.
13. APHA .(2000) Standard Methods for Examination of Water and Wastewater. 21st Edition. Washington, DC. American Public Health Association.
14. Davis, A.P., Shoukouhian, M., Ni, S. (2000). Loading estimates of lead, copper, cadmium and zinc in urban runoff from specific sources. *Chemosphere,* 44 :997-1009.