International Journal of Engineering & Technology, 7 (4.35) (2018) 219-222

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Heavy Metal Accumulation at the Bertam Agricultural Watershed in Cameron Highlands, Malaysia

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Abstract

The existence of heavy metals residues in water, soil and air poses a serious risk to all living organisms. Heavy metals, such as Cd, Pb, Cr, Ni, and Hg, are major sources of environmental pollution, especially in areas with high anthropogenic and agriculture activities. The objective of this study is to determine the status of heavy metal concentrations of Cd, Cr, Ni, Pb, Zn, Cu, and Fe in the water bodies of Bertam River, which passes through agricultural areas. The water samples were collected randomly in three replicates from 10 sampling points along the Bertam River. The heavy metals in the water were extracted by using filter paper with a pore size of 0.45 mm. The extracted water sample was preserved by adding nitric acid (pH <2). Sample concentrations were then tested for metal concentrations using inductively coupled plasma mass spectrometry. In this study, the highest mean concentration was Fe (96.04 ± 90.43 ppb), followed by Zn (5.68 ± 0.2.34 ppb), Cu (5.13 ± 2.98 ppb), Cr (1.53 ± 0.19 ppb), Ni (0.85 ± 0.22 ppb), Pb (0.85 ± 1.61 ppb), and Cd (0.027 ± 0.02 ppb), where Fe> Zn> Cu> Pb> Cr> Ni> Cd. However, the concentrations of selected heavy metals in the water samples were below the standards recommended by the World Health Organization.

Keywords: *Heavy metal; Cameron Highlands; pollutants; agriculture; water quality*

1. Introduction

Non-point source pollution in agriculture area is regarded as the most significant threat to the quality of surface water in rural areas [1-3]. The most critical route leading to the source of water pollution is runoff from the agricultural field [4]. The bioavailability of heavy metals can cause bioaccumulation in the food chain and can be very harmful to human health[5]. Runoffs from agricultural areas carry pesticides, heavy metal, soil, organic matter, manure and human waste into streams and rivers causing an increase in volume and change the water quality [5-7] especially in areas with high anthropogenic activities. Effects of runoff have been reported in detail by researcher [7-18]. Cultivation of vegetables in the highlands provides an opportunity for researchers to study the effects of agricultural runoff during pesticide and heavy metal applications on small rivers in the tropics.

Vegetable crops were recorded Cabbage, mustard, salad, tomatoes, Chinese Cabbage and other covers 28.4% of the land in Cameron Highlands, equivalent to 2140 hectares in 2013 [19]. Intensive agriculture activities created extensive drainage systems, where agricultural surplus water can flow into streams and rivers. The aquatic ecosystems that were in the river downstream from the agriculture area may be exposed due to the intensive use of pesticides, drainage and high rainfall tropical areas, particularly the highlands [20]. The study was conducted at Sungai Bertam in Cameron Highlands, Pahang. It flows from forest reserves and through major towns like Brincang and Tanah Rata and gathered at the Sultan Abu Bakar Dam. As such, the Bertam River is one of the main sources of water for nearby residences. Consequently, conservation and monitoring are very important to ensure that rivers are free of pollution. The objective of this study is to determine the status of heavy metal concentrations of Cd, Cr, Ni, Pb, Zn, Cu, and Fe in the water bodies of Bertam River, which passes through agricultural areas.

2. Material and Methods

2.1. Study Area

Pahang is the largest state in peninsular Malaysia which is covered by estimately 35,964 square kilometers land area and has an estimated total population of at 1,543,000 (Statistic Department, 2009). Pahang consists of eleven districts i.e Pekan, Rompin, Maran, Temerloh, Jerantut, Bentong, Raub, Lipis, Cameron Highlands and Bera as shown in Figure 1. Cameron Highlands District is the smallest district located at North West of Pahang. The district has divided into three mukim comprises Ringlet, Tanah Rata and Ulu Telom. The total area of Cameron Highlands districts is 712.18 square kilometres which bordered by Lipis district on the south-east, Kelantan on the north and Perak on the west. Cameron Highlands has experience a gradual increase in population over the years. The population growth rate was slightly below 2% per annum as compared to about 2.3% of average national growth rate.

2.2. Sampling Sites

Ten water quality monitoring station in Cameron Highlands (defines as Station 1-10) have been established in the intensive vegetable cultivation areas as shown in Table 1 and divided into three categorized which are upstream, middle and downstream (Figure 1).

Table 1: Description of Bertam River sampling locations in Cameron Highlands

Station	Longitude	Latitude
1	N04°30'17.0"	E101°23'14.7"
2	N04°29'30.1"	E101°23'12.5"
3	N04°29'14.4"	E101°23'4.3"
4	N04°28'49.9"	E101°22'50.2"
5	N04°28'44.7"	E101°22'54.5"
6	N04°28'18.0"	E101°22'54.0"
7	N04°27'58.4"	E101°23'10.1"
8	N04°27'5.4"	E101°23'29.1"
9	N04°26'34.40"	E101°23'17.20"
10	N04°25'52.70"	E101°23'16.40"

2.3. Sampling Procedure

In situ measurement: Physical water quality was measured in-situ using YSI model 550 multi-sensor probes for pH, temperature, conductivity, total dissolved solids and dissolved oxygen (DO). Calibration of YSI probes was conducted in the laboratory prior before field sampling and once again after sampling progress work was done. The meanwhile set sample of sediments was collected using scooped, and three replicates were taken from each station. Sediment samples were hence carefully collected using anti rust scoop, wrapped in aluminium foil and stored in a labelled polythene zipper bags before storing into the icebox. Finally, samples were transferred to the laboratory for further analysis.

2.4. Sampling

Sampling were carried out for different season which are dry season (May–July) and wet season (August–October). For each sample, I L volumes of surface water were collected in glass bottle for respective monitoring station. For BOD sample, the amber bottle were pre-rinsed before being filled just to overflowing. The sample were stored in cooled room before prior analysis.

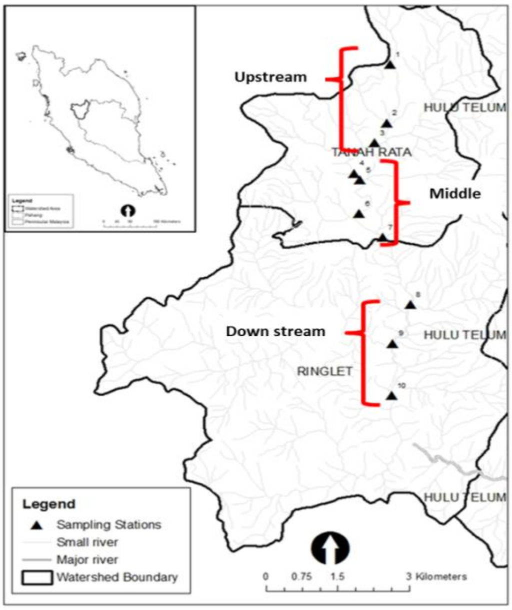

Fig 1: Map of Cameron Highlands showing the location of sampling stations

2.5. Sample Extractions and Analysis

Water samples were filtered using Nucleopore filter paper (0.45 mm). After filtered the water sample were preserved by adding HNO3 (pH <2). Detection of heavy metal was carried out using ICP-MS (PerkinElmer, USA). For Calibration curves analysis, multiple-level calibration standards by concentrations were calculated. 1000-mg/l stock solution was prepared for each heavy metal (MERCK Titrisol). Samples were filled in metal-free plastic tubes at room temperature for heavy metals detection [21].

3. Result and Discussion

The range of metal concentrations in river water samples were found as follows: Cd (0.0028-0.0002 ppb), Cr (0.12 to 0.55 ppb), Ni (0.02 to 0.17 ppb), Pb (0.07-0.74 ppb), Zn (0.03 -1.12 ppb), Cu (0:04 to 00:29 ppb) and Fe (48.18-409.50 ppb) (
Table **2**). Among the heavy metals studied Fe showed the highest concentration of 236.77 mg/ g followed by Zn (1.12 ppb), Cu (5.13 ppb), Pb (3.26 ppb), Cr (1.53 ppb), Ni (0.98 ppb) and Cd (0.03 ppb), (Fe> Zn> Cu> Pb> Cr> Ni> Cd).

Table 2: The range concentration selected heavy metals in water samples.

Heavy Metal	Range concentrations (ppb)
Cd	0.0028-0.0002
Cr	0.12-0.55
Ni	0.02-0.17
Pb	0.07-0.74
Zn	0.03-1.12
Cu	0.04-0.29
Fe	48.18-409.50

The concentration of heavy metals in water, as compared with values suggested by the Guidelines for Water Quality, Canada [22], Environmental Protection Agency, United States [23] that is for the maximum concentration (CMC) and a constant concentration (CCC) allowed for surface water without causing significant impacts to aquatic life and water quality interim national (INWQS) [24] as shown in Table 3.

Table 3: WHO safe limit and INWQS class to determine the quality of surface water

Heavy Metal	CCME-Protection of aquatic life (Freshwater) μg/L	EPA-Maximum concentration (CMC) μg/L	EPA 20/5000 Continuous concentration (CCC) μg/L	INWQS class II (μg/L)	WHO Limit μg/L
Cadmium (Cd)	0.017	2.0	0.25		3
Chromium (Cr)	-	-	-	50	50
Nikel (Ni)	25-150	470	52	50	-
Plumbum (Pb)	1-7	65	2.5	50	10
Zink (Zn)	30	120	120	120	-
Cuprum (Cu)	2-4	13	9.0	20	2000
Ferum (Fe)	300	-	1000	1000	300

Table 4: Sampling station according to the river section.

Sampling station	River part	Land use category
1, 2 & 3	Upstream	Forest and agriculture
4,5, 6 & 7	Midstream	Agriculture and urban areas
8,9 & 10	Downstream	Agriculture, urban areas and reservoir

In this study, the entire metal ion is below the CCME Guidelines, CMC, CCC and WHO. The highest mean concentration is, Fe (96.04 ± 90.43 ppb) showed the highest concentration of the total, followed by Zn (5.68 ± 0.2.34 ppb), Cu (5.13 ± 2.98 ppb),

Cr (1.53 ± 0.19 ppb), Ni (0.85 ± 0.22 ppb), Pb (0.85 ± 1.61 ppb) and Cd (0.027 ± 0.02 ppb) (
Table **5**).

All the stations were divided according to the particular part of the river (Fig 1 and

Table **5:** The analysis of metal concentrations in water samples selected at Sungai Bertam

Season	Value	Heavy metal (ppb) (Station) (Season)						
		Cd	Cr	Ni	Pb	Zn	Cu	Fe
Dry	Maximum	0.06 (10)	1.66 (10)	1.40 (9)	0.42 (8)	2.19 (9)	10.72 (1)	229.99 (8)
	Minimum	0.00 (6)	0.45 (1)	0.08 (1)	0.00 (4)	0.26 (1)	0.46 (2)	3.75 (1)
	Average	0.03 (10)	1.53 (10)	0.85 (10)	0.26 (9)	1.56 (10)	5.13 (7)	96.04 (8)
Raining	Maximum	0.03 (6)	0.58 (3)	0.98 (10)	3.26 (7)	7.52 (2)	4.27 (2)	236.77 (2)
	Minimum	0.00 (10)	0.05 (1)	0.10 (1)	0.01 (4)	0.01 (7)	0.03 (7)	0.56 (7)
	Average	0.02 (8)	0.45 (8)	0.82 (10)	0.85 (7)	5.68 (3)	2.48 (10)	70.45 (2)
	Average max both season	0.03 (8) (dry)	1.53 (10) (dry)	0.85 (10) (raining)	0.26 (9) (dry)	5.68 (3) (raining)	5.13 (7) (dry)	96.04 (8) (dry)
	Average min both season	0.00 (10) (raining)	0.05 (1) (raining)	0.08 (1) (dry)	0.00 (4) (dry)	0.01 (7) (raining)	0.03 (7) (raining)	0.56 (7) (raining)

). The highest concentration of Fe, Pb, Zn, Ni and Cr were all located in the downstream river station (station 8, 9 & 10). Station 10 has received many sources of pollution in Sungai Bertam because it is found in the lower river and a dam that reflects the accumulation of river water as sediment samples. Besides, the station is an area downstream of agricultural and urban areas. While the highest average concentration of Cu is located in the midstream part of the sampling station 7. The midstream part of the river is farmland and urban areas. For Zn also record the highest average in the upper stream at station 3.

Table 5: The analysis of metal concentrations in water samples selected at Sungai Bertam

Season	Value	Heavy metal (ppb) (Station) (Season)						
		Cd	Cr	Ni	Pb	Zn	Cu	Fe
Dry	Maximum	0.06 (10)	1.66 (10)	1.40 (9)	0.42 (8)	2.19 (9)	10.72 (1)	229.99 (8)
	Minimum	0.00 (6)	0.45 (1)	0.08 (1)	0.00 (4)	0.26 (1)	0.46 (2)	3.75 (1)
	Average	0.03 (10)	1.53 (10)	0.85 (10)	0.26 (9)	1.56 (10)	5.13 (7)	96.04 (8)
Raining	Maximum	0.03 (6)	0.58 (3)	0.98 (10)	3.26 (7)	7.52 (2)	4.27 (2)	236.77 (2)
	Minimum	0.00 (10)	0.05 (1)	0.10 (1)	0.01 (4)	0.01 (7)	0.03 (7)	0.56 (7)
	Average	0.02 (8)	0.45 (8)	0.82 (10)	0.85 (7)	5.68 (3)	2.48 (10)	70.45 (2)
	Average max both season	0.03 (8) (dry)	1.53 (10) (dry)	0.85 (10) (raining)	0.26 (9) (dry)	5.68 (3) (raining)	5.13 (7) (dry)	96.04 (8) (dry)
	Average min both season	0.00 (10) (raining)	0.05 (1) (raining)	0.08 (1) (dry)	0.00 (4) (dry)	0.01 (7) (raining)	0.03 (7) (raining)	0.56 (7) (raining)

The highest average value Cu was recorded at station 7 and ten during the rainy season and the dry season, which is close to densely populated urban areas with population, probably due to domestic sewage and runoff from intensive farming areas [25]. Increased Cd (only slightly) in the dry season may arise from the use of fertilisers to improve the quality of crops. Also, increasing Cd result from the action of weather on natural rock (rock of granite). The pattern shows a slight increase in Cd accumulation in the water during low flow conditions of rivers in the dry season [26]. Pb concentrations were higher in the dry season in streams may be due to acidic drainage of industrial wastes and mineral Pb. Pb can be carried in water, either dissolved or as water-borne particles. However, some lead compounds are dissolved in water, although most of Pb is then settles on the surface of the water channel [27]. ANOVA statistical test showed that heavy metal selected in this study differ significantly between stations (P <0.05). The results suggest that the variation of metal contamination is strongly influenced by the location, especially in Sungai Bertam downstream area near the dam area.

During raining season, the Fe (236.7 ppb) recorded the highest average value of heavy metal at station 2 (upstream). Fe contaminants may come from agricultural activities from point and non-point-sources. Among the metals studied, Fe is the metal found in the highest concentration average for the entire study. It is not surprising because Fe is the fourth most common element in the crust [28].

4. Conclusions

Heavy metal pollution occurring along Sungai Bertam was localised which are concentrated at midstream and downstream river. Agricultural activities and the impact of the on-going urbanisation have the effect of increasing concentration of Cd, Cr, Ni, Pb, Zn and Cu, especially in the dry season in the water samples causing pollution along Sungai Bertam Right. The concentration of metals in water sample is Fe> Zn> Cu> Pb> Cr> Ni> Cd. However, the concentration of heavy metals was selected in this study water samples were below the CCME Guidelines, CMC, CCC and WHO. In conclusion, the runoff from the agriculture area, the impact on the midstream and lower reaches of the river.

Acknowledgements

The authors would like give special appreciation goes to the Department of Agriculture, Cameron Highlands (through the Ministry of Agriculture), and the Ministry of Education (My Brain 15) for supporting this research.

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