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Heavy metal and insecticide distribution and accumulation at the Bertam Agricultural Watershed in Cameron Highlands, Pahang, Malaysia

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ABSTRACT

This study aimed to determine the status of heavy metal concentrations of Cd, Cr, Ni, Pb, Zn, Cu, and Fe in the water bodies of Bertam River, Cameron Highlands, which traverses agricultural areas. Water samples were randomly collected in three replicates from 10 sampling points along the river. Then, the samples were tested for metal concentrations using inductively coupled plasma mass spectrometry. The insecticides cypermethrin and chlorpyrifos, which are widely used by farmers, were analyzed. The water samples were drawn into a C_{18} cartridge. Cypermethrin or chlorpyrifos absorbed by the cartridge were extracted using 6 mL of acetone and then injected into the gas chromatography–electron capture detector. 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); hence, 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 WHO. The overall average concentrations of chlorpyrifos and cypermethrin in the dry season ranged from 0.40 ppm to 2.37 ppm and from 0.001 ppb to 0.13 ppb, respectively. By contrast, the overall average concentrations in the rainy season ranged from 0.04 ppm to 0.80 ppm and from 0.00 ppb to 0.010 ppb, respectively. Results showed that runoff from the agricultural area affected water quality.

1.INTRODUCTION

Runoff from agricultural areas carry pesticides, heavy metal, soil, organic matter, manure, and human waste into streams and rivers, increasing their volume and changing the water quality [1] especially in areas with high anthropogenic activities. Vegetable farming in the Cameron Highlands provides researchers the opportunity to examine the effects of agricultural runoff on small rivers in the tropics during the application of pesticides and heavy metals.

Intensive agricultural activities involve an extensive network of drainage systems, where agricultural surplus water can flow into streams and rivers. River aquatic ecosystems that are downstream from an agricultural area may experience exposure related to the intensive use of pesticides, drainage, and high tropical rainfall, particularly in regions such as the highlands. Consequently, this study was conducted at Sungai Bertam in the Cameron Highlands, Pahang. The objective of this research was 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 traverses agricultural areas.

2. MATERIALS AND METHODS

2.1 Study Area The Cameron Highlands, situated in the state of Pahang, has an estimated area of 712 km^2. It is one of the significant agricultural areas for both domestic and export markets. The average temperature recorded at the Cameron Highlands is about 17.9 °C, and the mean minimum temperature is about 15.3 °C.

2.2 Sampling sites

Ten sampling sites for surface water were selected along Bertam River. The sites were divided into 10 sampling points along the river (Upstream Stations 1–3, Midstream Stations 4– 7, and Downstream Stations 8–10). All the sampling sites were located in intensive vegetable cultivation areas.

2.3 Sampling Procedure

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 the YSI probes was conducted in the laboratory prior to and after field sampling. Meanwhile, a sample set of sediments were collected with a scooper, and three replicates were taken from each station. Finally, samples were transferred to the laboratory for further analysis.

2.3.1 Sampling

Seasonal field samplings were carried out during the dry season (May–July) and wet season (August–October) throughout the six-month period in 2014. Three replicates of 1 L water were collected in glass bottles from each sampling site. In situ measurements (pH, temperature, DO, salinity, and conductivity) were taken prior to storing the samples in 1 L amber glass bottles. The containers were pre-rinsed with the river water sample before being filled just to overflowing. Samples reached the laboratory 1 day after sampling, and were stored at 48 °C prior to extraction, normally within 48 h.

2.4 Sample extractions and analysis

2.4.1 Determination of Insecticide

Solid-phase extraction (SPE) and chromatographic techniques were applied to quantify the pesticides. The collected samples were pre-filtered on 0.45 mm HVLP filters (Millipore Bedford, MA, USA) to eliminate particulate matters. Prior to the extraction, the C bonded phase (J.T. Baker) and poly (styrene–divinylbenzene) disks of 47 mm diameter and 0.5 mm thickness and containing 500 mg of the bonded phase were washed with 10 ml of acetone under vacuum followed by 3 mL of acetonitrile and 3 mL of distilled water. The disks were not allowed to dry, as recommended [2]. The samples were mixed well and allowed to percolate through the disks at a flow rate of 1.5 ml/min under vacuum. SPE tubes were immersed in the water samples and the pump was turned on. During inhalation, the water samples were drawn into the C_{18} cartridge. Water flow through the SPE cartridge was controlled using the pressure knob, such that the pressure drop of the extracted water samples was drop by drop. After extraction, pesticide residues trapped in the disk cartridge were collected by using 6 ml of acetone as the eluting solvent. The fraction was evaporated to 1 mL by vacuum before being injected into the Gas chromathography fitted with electron capture detector (GC-ECD). Three replicates were carried out for each sample, and 1 µL of the sample was injected twice with each replication [3].

2.4.2 Determination of Heavy Metals

Samples were then filtered, and the heavy metals were determined using ICP-MS (PerkinElmer, USA). Calibration curves were analyzed using multiple-level calibration standards by concentrations and then calculated. A 1000 mg/l stock solution was prepared for each heavy metal (MERCK Titrisol). Samples were stored in metal-free plastic tubes at room temperature until the determination of heavy metals [4].

3. RESULTS AND DISCUSSION

3.1 Heavy metals

The ranges of metal concentrations in the river water samples were as follows: Cd

(0.0028–0.0002 ppb), Cr (0.12–0.55 pbb), Ni (0.02–0.17 pbb), Pb (0.07–0.74 pbb), Zn (0.03– 1.12 ppb), Cu (0.04 to 00.29 pbb), and Fe (48.18–409.50 pbb). Among the heavy metals studied, Fe showed the highest concentration at 236.77 ppb, followed by Zn (1.12 pbb), Cu
(5.13 pbb), Pb (3.26 pbb), Cr (1.53 pbb), Ni (0.98 pbb), and Cd (0.03 pbb); specifically, Fe>

Zn> Cu> Pb> Cr> Ni> Cd.
The highest concentrations of Fe, Pb, Zn, Ni, and Cr were all located in the river downstream station (Stations 8–10). Station 10 (dam) received numerous sources of pollution of Bertam River because it is located in the lower river and in a dam that reflects the accumulation of river water as sediment samples. The highest values of Cu during the rainy and dry seasons were recorded at Stations 7 and 10, respectively, probably due to runoff from intensive farming areas and domestic sewage (both stations are close to densely populated urban areas) (Table 1). A slight increase in Cd during the dry season may be attributed to the use of fertilizers to improve the quality of crops [5]. Pb concentrations were higher in the dry season likely because of the acidic drainage of industrial wastes and mineral Pb. Pb can also be carried in water, either dissolved or as water-borne particles. Cr and Ni showed higher concentrations during the dry season. Conversely, Zn concentration was higher during the rainy season. Among the studied metals, Fe was found to have the highest concentration.

Table 1 Analysis of metal concentrations in water samples from Bertam River

Season	Value	Metal (ppb) (Station)						
		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)	229.59 (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)
	Max. Average	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 (6) (dry)
	Min. Average	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)

Note: Brackets indicate the station numbers or the seasons when samples were obtained.

3.2Insecticide

Pesticide concentrations during the dry and rainy seasons are summarized in Table 2. Insecticide was found in the upper stream, midstream, and downstream reaches of Bertam River, and pesticide residue was present during both seasons.

Table 2 Mean concentrations (± SE; n = 3) of pesticides in the water at Sungai Bertam (ug/L) with a statistical difference between the sampling periods (ANOVA)

Sampling Periods	Upstream		Midstream		Downstream	
	Cypermethrin (n = 10)	Chlorpyrifos (n = 18)	Cypermethrin (n = 24)	Chlorpyrifos (n = 24)	Cypermethrin (n = 18)	Chlorpyrifos (n = 18)
Dry Season	0.005±0.006	0.502±0.624	0.008±0.009	0.450±0.660	0.007±0.006	1.123±1.955
Rainy Season	0.005±0.06	0.261±0.700	0.003±0.002	0.233±0.32	0.002±0.001	0.509±0.710
p-value[a]	0.000*	ND	0.00*	0.004*	ND	ND

Note: ND= not detected

Water samples from the upstream, midstream, and downstream sections taken during the rainy season and under the influence of runoff showed very low concentrations of cypermethrin (> 0.01 mg/L). Relatively increased water pollution by chlorpyrifos (0.261, 0.233, and 0.509 µg/L) was detected in the upstream, midstream, and downstream sections, respectively, in the same sample from the rainy season. Cypermethrin pesticide concentrations measured in the rainy season from the midstream of the river increased significantly ($p \leq 0.005$) from its concentrations during the dry season.

Runoff from agricultural areas contains pesticides [1] and carries sediments [6]. Research has linked the effect of such runoff to the current use of pesticides along Sungai Bertam. This effect is evident from the comparison between the upper, midstream, and lower reaches of the river before and after the rain. Agricultural runoff affects the quality of the river downstream. Moreover, agricultural areas dominate the whole catchment of the river from upstream to downstream. Although pesticide concentration in the dry season is higher than in the rainy season, the concentration is constantly elevated. High concentrations of pesticides detected in the water in the entire sub-catchment of the river during the rainy season sampling

indicate that the effect of agricultural runoff can be detected in a small river. The release of the pesticide remains could not be identified because no definite evidence was found in this study.

4.CONCLUSIONS

Heavy metal pollution along Sungai Bertam was localized and concentrated midstream and downstream. Agricultural activities and ongoing urbanization increased the concentrations of Cd, Cr, Ni, Pb, Zn, and Cu. In this study, the differences in the level of pesticides in the river were shown, with a focus on the comparison of the upper, midstream, and lower reaches of the river before and after the rainfall followed by runoff from the agricultural area. Differences in agricultural activities in the upstream and downstream sub-catchment may cause variations in the pesticide contamination among the sampling locations.

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