Time Series Analysis of Heavy Metal Concentrations along the Watershed Gradient in Cameron Highlands: Geospatial Approaches.

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Abstract. Heavy metal, particularly cadmium, lead, and arsenic, constitute a significant potential threat to human health. Some metals are extremely toxic to humans and the toxic heavy metals of greatest concern include cadmium, lead, and arsenic. The objective of the study conducted was to determine the accumulation and distribution status of heavy metal cadmium (Cd) in the sediment of Bertam River from September 2014 to February 2015 in the agricultural areas of Cameron Highlands, Malaysia. The sediment samples were collected randomly in three replicates from ten sampling points in the agricultural areas of Cameron Highlands. The heavy metals in the sediment were extracted using the wet acid method and the sample concentrations are then tested for metal concentrations by the spectrography method using Inductively Coupled Plasma (ICP) spectrography. Inverse distance weighting (IDW) was used to create a map of metal concentrations for a point on the polygon dataset spatial interpolation. There is an increasing trend of Cd from the upstream to downstream stations along Bertam River during the rainy season. The activity range of Cd is 0.07 to 2.83 µg/g during the rainy season, whereas, during the dry season, Cd activity ranged from 0.26-0.83 µg/g.

1. Introduction

The presence of heavy metals traces in the atmosphere, soil, and water can cause serious problems to all organisms and the ubiquitous bioavailability of these heavy metals can result in bioaccumulation in the food chain that can be highly dangerous to human health [2, 3, 5, and 6]. Traces of heavy metals, such as arsenic, cadmium, lead, chromium, nickel, and mercury are key environmental pollutants, particularly in areas with high anthropogenic pressure [3]. The objectives of this study were to examine the status of heavy metal concentrations cadmium (Cd) in agricultural areas and to evaluate the factors that contribute to its accumulation.
The study was conducted along Bertam River in Cameron Highlands, Pahang. The river flows from Forest Reserve in the north, passing through the valley to the south and ends at Sultan Abu Bakar Dam. Bertam River is also the source of drinking water for the residents nearby. Therefore, conservation and ongoing monitoring is necessary to ensure that the river is free from pollution.

2. Materials and Methods

2.1 Sampling

Along the Bertam River, ten sampling points were selected with the location and activities of the surrounding land use recorded, as shown in Figure 1 and Table 1. Sediment samples were collected using a stainless steel scoop and replicated 3 times from each station from September 2014 to February 2015. The sediment samples were carefully wrapped using aluminium foil and put in a labelled polythene zipper bag before storing them in a cooler box.

![Figure 1: Sampling Location](image)

![Figure 2: Rainfall trends from May 2014 to April 2015](image)

| No. | Longitude   | Latitude   | Land use   |
|-----|-------------|------------|------------|
| 1   | N04°30'17.0"| E101°23'14.7" | Forest   |
| 2   | N04°29'30.1"| E101°23'12.5" | Orchard  |
| 3   | N04°29'14.4"| E101°23'43"  | Rangeland |
| 4   | N04°28'49.9"| E101°22'50.2" | Forest  |
| 5   | N04°28'44.7"| E101°22'54.5" | Urban area |
| 6   | N04°28'18.0"| E101°22'54.0" | Forest  |
| 7   | N04°27'58.4"| E101°23'10.1" | Urban area |
| 8   | N04°27'5.4" | E101°23'29.1" | Orchard  |
| 9   | N04°26'34.40"| E101°23'17.20" | Orchard |
| 10  | N04°25'52.70"| E101°23'16.40" | Lake   |

The samples were then filtered and determination of Cd was carried out using an air–acetylene flame atomic absorption spectrophotometer (AAS) Perkin-Elmer Model 4100. Output data are presented in µg/g dry weight (dw) basis. Calibration curves were analysed using multiple-level calibration standards by concentrations and calculated. 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 was conducted using ICP-MS (PerkinElmer, USA) [2]. Inverse distance weighting (IDW) was used to create a map of metal concentrations along the watershed gradient for a point on the polygon dataset spatial interpolation.
2.2 Rainfall Data
Monthly rainfall data of Cameron Highlands from May 2014 to April 2015 were obtained from the Department of Irrigation and Drainage (DID) as shown in Figure 2. During dry season (January to April 2015) sampling period, the rainfall recorded in Cameron Highlands was between 150-170 mm. Meanwhile, during the rainy season (September to December 2014), a scale ranging from 243-388 mm of total rainfall was recorded.

3. Results and Discussion
The concentrations of heavy metal Cd in the water at the 10 sampling stations areas shown in Figure 3. This study shows that the concentration of Cd in Bertam river basin is between 0.07 to 2.83 µg/g. The concentration of heavy metals in water were compared with the Guidelines for Air Quality, United States [4] which allowed or maximum concentration (CMC) and a constant concentration (CCC) to the surface water without causing significant impact to aquatic wildlife. The results showed that the Cd concentrations found in all stations are low and do not exceed the recommended maximum concentration (EPA CMC 2 µg/g) except for S10 during the wet season.

The concentration of Cd showed an increasing trend at all locations (Figure 3) from July 2014 to November 2014 especially at station 10, which is located at Sultan Abu Bakar Dam (0.07 µg/g, lowest value; 2.83 µg/g, highest value). This could be due to the authorities wanting to ensure that the water level is lower than the intake depth to facilitate excavation of sediment in the lake. The results also showed that S10 recorded the highest range and mean of concentration activity of Cd as obviously seen in Fig.3. This is because S10 is located near the mouth of the river connected by a dam and indirectly there are additional sediment inputs from agriculture, farming and industries in the upstream areas of small rivers.

![Figure 3: Concentration of Cadmium from July 2014 to March 2015](image)

Other than S10, during dry season, S5 (1.79 µg/g) and S7 (1.49 µg/g; 1.42 µg/g) concentrations of Cd are higher than the other locations where the same pattern of Cd occurred. The concentration was slightly higher than other stations, indicating there is an accumulation of Cd due to the circulation of water at the outlet of the river. All stations show the similar concentration profile for Cd with the exception of S5, S7 and S10, which showed a higher concentration (Figure 3). Cd is insoluble in water and is usually associated with solid material [7]. Due to the additional input from a small river that connects to S10, Cd in the form of suspended solids will gather at the river junction. The confluence of two rivers will increase the Cd content in the sediment itself. The trend of Cd concentrations that were higher at S5 and S7 can also be observed at S10 can be attributed to the same cause.
Figure 4: Concentrations of heavy metal (Cd) along the watershed gradient from July 2014 to March 2015
The concentrations of heavy metal (Cd) along the watershed gradient from July 2014 to February 2015 are as shown from figures 4 to 10 (Figure 4). As the slope decreased along Sungai Bertam, the concentration of Cd increased during the rainy season especially at S10. This might be due to heavy rainfall, increased agricultural activities where all the sediment inputs of pesticides and fertilizers enter the river. Moreover, land use features also contributed to sediment input for Cd. As in this study, S10 is located at the lowest point, which is also known as the Sultan Abu Bakar Dam, where all the runoff sediment accumulated and this will lead to increased concentrations of Cd in the event of heavy rain. As for the dry season, the trend decreased starting from January to April 2015.

4. Conclusion
This study concluded that in general, concentrations of heavy metal, Cd in the water of the research area of Bertam River Basin is low except for S10 where there is an increasing trend, especially in areas where there are anthropogenic activities such as agriculture and industry. There is an increasing trend of Cd from upstream to downstream stations of Bertam River during the rainy season. Determination of Cd was established by using alpha spectrometry. The activity range of Cd is from 0.07 to 2.83µg/g during rainy season, while for dry season the Cd activity ranged from 0.26 to 0.83µg/g.

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