THE IMPACT OF THE APPLICATION OF AGROCHEMICALS ON HEAVY METAL POLLUTION IN PLANTATION AREA

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Abstract

The application of agrochemicals in plantation activities has a potential to pollute the surrounding areas with some levels of heavy metals. The study was conducted to measure the heavy metals content deposited around the site and to evaluate the pollution indexes of the area. The observation obtained was further used to evaluation of the impact of agrichemicals on the surrounding. The mosses and soil samples were digested using a wet digestion method and the heavy metals were analysed by using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). Four physicochemical parameters including temperature, dissolved oxygen (DO), pH and specific conductance (SpC) were measured *in situ*. The mean metal concentration order for the moss sample was observed as Zn > Cu > Cr > Ni > Cd > Pb while in the order of Pb > Zn > Cr > Cu > Ni > Cd for the topsoil. For surface water sample, the order of metal concentration was Zn > Pb > (Cd = Cr = Cu) >Ni. The Contamination Factor (CF), Pollution Load Index (PLI) and correlation pair analysis derived from the measured data clearly proved that all samples of mosses, topsoil and surface water have been polluted by the selected heavy metals studied.

Keyword: Moss, Top Soil, Surface Water, Heavy metal, Contamination factor, Pollution Load Index.

Introduction

The agricultural industry is a dominant industry that supports most of the human essentials especially food. The growth of agriculture products depends mostly on the population. The successfulness of the agricultural industry is supported by the use of sophisticated agricultural technology to fulfil the farmers' desire and increase their productivity (Antle et al., 2017). The production of agrochemicals is formulated based on the certain problems faced by the farmers. Despite the rapid development of the agricultural industry worldwide, there are several problems arise due to activities of this sector toward human and the surrounding environment. According to Perlatti et al. (2013), improper agriculture practices will give a huge negative impact on the environment and emit the various types of environmental pollutants. The increase in world population forces the limits of agricultural area and leads to the excessive use of agrochemicals. The increase in consumption of fertilizers and the application of the agrochemicals potentially pollutes the environment. Agrochemicals are highly toxic and have been associated with serious human health and environmental damages (Briggs and Courtney, 1989). The active consumption of toxic agrochemicals such as phosphate fertilizer will contaminate soil and water with heavy metals, pesticides, and herbicides (Lin et al., 2010). In general, some metals are present in trace amount in the environment but possibly can give harmful effects to human. Natural resources such as soil, water, and air should be preserved for the benefit of our future generation. Heavy metals that contaminate the soil have been proved to inhibit the soil microbial activities by either decreasing the soil fertility or inhibiting the germination of selected seeds. Contamination of soil by heavy metals will affect the balancing of nutrients in plants with negative effects on the functioning and synthesis of abundant biological active compounds (Etim and Onianwa, 2012). A study by Wong et al. (2002), showed the presence of heavy metals such as Co, Cr, Cu, Ni and Zn in agricultural soil.

In Malaysia, Jengka agricultural territory is considered as one of the biggest FELDA residence sites located in Pahang. The area of Jengka agricultural territory is surrounded by fertile soil (Wikkramatileke, 1972) which is suitable for plantation activities especially for oil-palm and rubber. After operating for a long time in plantation and related activities, it is important for the local authority of the area to monitor and periodically measure the level of the contaminants that possibly has been released by agricultural activities to the surrounding areas. This study has been conducted to measure the distribution of the heavy metals content deposited surrounding the selected area and to evaluate the pollution status based on contamination factor (CF) and pollution load index (PLI). The results obtained also compared to the guidelines and limits set by the WHO and the data could be used by the local authority to formulate appropriate agricultural policies.

Materials and Methods

Study Area

The study was carried out along Chenerai River site which is located in the middle part of the Jengka Triangle agricultural area in Pahang, West Malaysia with the latitude 3° 45’0” N and 102° 33’ 0” E.

Analysis of the Soil Samples

Soil samples were collected according to Abdullah et al. (2014) with minor modification to adapt to the local sampling area topography. A total of 12 topsoil samples (0 - 20 cm in depth) were collected along the riverside by using hand-auger. The samples were stored in polyethylene bags for transport and storage. The topsoil samples were air-dried in a clean and isolated area in a laboratory for three days. The samples were sieved to remove large debris, stones, pebbles, and any unwanted materials. Finally, the samples were grounded in a mechanical agate grinder until fine particles (< 200 µm) were obtained.

Wet acid digestion was applied to prepare the topsoil sample in liquid form. 1.0 g of each sample was accurately weighed for aqua regia (HCl: HNO_3, 3:1 solution) digestion. The mixture was then heated on a hot plate until the sample was almost dry and then cooled to room temperature. This procedure was repeated with another 10 mL of 5% concentrated HNO_3 to re-dissolve the residue. The extracts were then filtered into 50 mL volumetric flask and brought up to volume with deionized water. Replicate extracts of each sample, were prepared (Yekeen and Onifade, 2012).

Moss Samples

Moss samples were collected in an open area and at least 100 m away from the main road (Harmens et al., 2013). Two most abundant mosses species grow around the area were collected, *Syrrhopodon Ciliates* and *Arthrocormus schimperi* from 12 sampling stations scattered around the study area. The moss samples grown 0.8 meter from the ground on palm oil trees trunk were taken by using the ceramic blade constantly cleaned to remove the remaining previous mosses in order to avoid cross-contamination.

The dead materials and litter were removed from the samples and the only green parts of the moss segments were analysed. The clean moss samples were dried at 40 °C overnight and grounded in a mechanical agate grinder until fine particles (< 200 µm) were obtained (Abdullah et al., 2011). The accurate 0.5 g of mosses samples and 10 mL of freshly prepared aqua regia were mixed. The mixture was heated on a hot plate for 20 minutes and cooled down to room temperature; 20 mL of deionized water was added. Finally, the solution was filtered and diluted to the mark (Ansari et al., 2004).

Water Samples

Water samples were collected from upstream to downstream of the river at an interval of 100 meters between consecutive sampling stations. The water samples were collected at a level of an approximately 20 cm below the water surface (Varol & Sen 2012). The water samples were analysed for their selected *in situ* parameters and the metals content.

The concentrations of the heavy metals were measured by Inductively Coupled Plasma Optical Emission Spectrometer, ICP OES (5100 Agilent Technologies). For quality assurance, standard reference materials SRM – CC141 were prepared and analysed with the same procedure and reagents. All metal concentrations were covered in a range from 80 to 110 %. This would suggest that the analytical procedure applied in this study was reliable and acceptable.

Results and Discussion

Metal deposition around agriculture area

The concentrations of the deposited heavy metals in this area were varied among the different types of environmental samples (**Table 1**) may be attributed to differential absorption capacities of different types of samples for different metals (Kayastha, 2014). Deposition and accumulation of metals in lower plants, soil and surface water around agricultural sites would be influenced by various atmospheric factors and conditions especially the types of pesticides and fertilizers applied, weather conditions and the irrigated water. The results of this study showed that the metal contents in all different sample types were unevenly distributed in the area. In general, most of the mean metal contents were found higher in the soil sample compared to in plants and water except for Ni (**Table 1**).

In topsoil samples, the highest mean concentration was observed for Pb with 39.83 mg/kg followed by Zn, Cr, Cu, Ni and Cd which recorded 27.54, 22.38, 19.04, 5.58 and 1.13 mg/kg respectively. In general, all the measured metal contents in topsoil were within the threshold values as recommended by WHO except for Cd which was 41.3 % higher than the recommended value. Zn was observed with the highest concentration in moss with 25.0 mg/kg followed by Cu, Cr, Ni, Pb and Cd with 14.67, 13.46, 6.0, 5.69 and 0.05 mg/kg respectively. Almost all metal concentrations observed in moss were lower compared to metal contents observed in topsoil except for Ni which recorded 7.2 % higher. Based on the threshold values set by the WHO for plants, Zn, Pb, Cu, and Cd were observed exceeding the suggested limits.

The difference in accumulation period possibly had influenced the data where the total heavy metal contents in moss would reflect the three years' accumulation process. This finding is similar to what was observed by Fernandez and Carballeira (2001).

Table 1 Concentration of heavy metals in topsoil, moss and surface water

Metals	Concentration Mean ± SD			*WHO (mg/kg) Plant	*WHO (mg/kg) Topsoil	**WHO (mg/L) Water
	Moss (mg/kg)	Topsoil (mg/kg)	Surface water (mg/L)			
Cd	0.05 ± 0.00	1.13 ± 0.34	1.00 ± 0.00	0.02	0.8	0.01
Cr	13.46 ± 5.38	22.38 ± 3.87	1.00 ± 0.00	1.30	100	0.10
Cu	14.67 ± 3.24	19.04 ± 17.25	1.00 ± 0.00	10.00	36	2.00
Ni	6.00 ± 2.09	5.58 ± 1.41	0.10 ± 0.00	10.00	35	0.20
Pb	5.69 ± 2.24	39.83 ± 11.89	1.89 ± 0.32	2.00	85	5.00
Zn	25.0 ± 7.91	27.54 ± 4.29	3.73 ± 0.83	0.60	50	3.00

** WHO permissible limits for heavy metals in plant and soil (WHO, 1996)*
*** Recommended maximum concentrations of trace elements in river water (WHO, 2005)*

The highest metal concentration in surface water samples was Zn with 3.73 mg/L and the lowest was Ni which recorded 0.1 mg/L. The concentration of Cd (1.0 mg/L), Cr (1.0 mg/L) and Zn (3.73 mg/L) in the surface water samples were found higher than the suggested WHO permissible values. The low dissolving ability of metals in water possibly has caused the low concentration of metals in river water compared to the topsoil and plants. The high rate of water flow and weather conditions also plays important roles in influencing the metal concentration in river surface water.

The high concentration of Cd in topsoil, moss and surface water samples in the study strongly suggests the possible effect of the consumption of agrochemicals such as phosphate fertilizers (Raymond and Okieimen, 2011), pesticides and herbicides in the study area (Huang et al, 2007).

Cadmium (Cd) is known as an extremely dangerous element that potentially gives adverse effects to human health causing kidney damage and bone defects (Ogundele et al., 2015). In this study, the mean concentrations of Cu in topsoil and surface water were observed lower than the permissible limit set by WHO but in moss samples, it recorded 46.7 % higher than the permissible limit. The use of fungicidal spray (high Cu content) and copper sulphate to improve soil fertility possibly had enriched the Cu concentration in moss samples (Mico et al., 2007). The low Cu concentration in topsoil in the study area possibly influenced by the dense cow grass in the surrounding area and leached away by the rainwater. The presence of Pb in environmental substrates is normally originated from natural activities and vehicular emission. In this study, the concentration of Pb in topsoil and surface water were within the permissible limit set by WHO but not in moss samples which recorded 1.85 times higher than the limit. Relatively weak molecular binding of Pb in the topsoil layer and high solubility in water possibly leached out the metal from the substrates.

Physicochemical Parameters

The results of the physicochemical parameters of surface water sample are summarized in **Table 2**. pH is a measure of the hydrogen ion concentration in water. Drinking water with a pH between 6.5 and 8.5 is generally considered satisfactory. In this study, the mean (from 12 sampling points) pH measured was 4.32 indicating the water was slightly acidic. This value exceeded the permissible WHO value which will cause harmful effect to the habitats especially to the aquatic habitat. The application of fertilizers to acidify the soil and leached out to the river through the subsurface flow process is probably the main factor that increased the water pH (Katimon et al., 2004).

Table 2 Physicochemical parameters of surface water in the study area

Parameters	Average value ± SD
Temperature (°C)	25.72 ± 0.07
pH	4.32 ± 0.13
Dissolved Oxygen (DO)(mg L^{-1})	4.87 ± 0.73
Conductivity (µS cm^{-1})	72.00 ± 0.00

Electrical conductivity is the ability of water to carry an electric current caused by the presence of dissolved solids such as calcium, chloride, and magnesium in water. The measured mean conductivity value of the water sample in this study is 72.0 µS cm^{-1}. The maximum allowable level of conductivity is 1000 µS/cm^{-1} (Hakanson, 1980). The difference in conductivity is influenced by various factors such as agricultural and industrial activities and land use, affecting the mineral contents and thus the electric conductivity of the water (Turekian and Wedepohl, 1961). Conductivity does not have a direct impact on human health. It is determined for several purposes such as mineralization rate (existence of minerals such as potassium, calcium, and sodium) and estimation the number of chemical reagents used to treat water. High conductivity may lead to lowering the aesthetic value of the water by giving mineral taste to the water. Typically, most of freshwater conductivity is ranging from 10 – 1000 µS cm^{-1} unless the water sources are receiving an extremely high level of pollutants; the conductivity can exceed 1000 µS cm^{-1} (Wilson, 2012).

Dissolved oxygen level should be adequate to support desirable aquatic life. Total dissolved oxygen concentration in water should not exceed 110 percent where above this level it can be harmful to aquatic life. Despite the need for oxygen by fish and other aquatic organisms to live, dissolved oxygen also plays an important role in the precipitation and dissolution of organic substances in water. In this study, the mean value of dissolved oxygen was measured as 4.87 mg/L which is considered good for aquatic organisms especially fish. If the concentration of dissolved oxygen were lower than 2.00 mg/L, most of aquatic live were dead in a day. Based on National Water Quality Standards (NWQS) for Malaysia and DOE Water Quality Index Classification, the studied river water could be classified as Class III which indicates the water would require extensive treatment in order to meet water quality standards.

Contamination Factor (CF) and Pollution Load Index (PLI)

To assess and quantify the level of the selected metals in the area, contamination factor (CF) and pollution load index (PLI) were used. The index of contamination factor, CF, was calculated according to Hakanson (1980) which stated as:

$$CF = (C_{metal}) / (C_{background})$$

Where; CF is a contamination factor of the metal of interest; ($C_{background}$) is the background concentration; and (C_{metal}) is the concentration of the metal. Contamination factor has six categories: < 1 no contamination; 1 - 2 = suspected; 2 – 3.5 slight; 3.5 – 8 moderate; 8 – 27 severe; above 27 = very high contamination. The world mean concentration of Cu (45 µg/g), Ni (68 µg/g), Mn (900 µg/g), Pb (20 µg/g), and Cd (0.3 µg/g) reported for shale were considered as the background value (Turekian and Wedepohl, 1960). For each contaminant, the PLI was calculated using the equation proposed by Wilson (2012).

$$PLI = \sqrt[n]{(CF_1 \times CF_2 \times \ldots \times CF_n)}$$

If PLI < 1, it indicates no pollution of the area whereas if the PLI > 1, then it indicates the area is polluted.

Table 3 Contamination factor (CF) and Pollution load index (PLI) in topsoil, moss and surface water

	CF						**PLI**	**Indication**
Parameter	Cd	Cr	Cu	Ni	Pb	Zn		
Water	20.0	20.0	20.0	2.0	38.0	1.33	3.06	Polluted
Soil	2.26	2.36	3.17	1.64	2.57	1.62	2.21	Polluted
Moss	1.00	1.12	2.45	2.00	1.57	1.15	1.46	Polluted

Contamination factors (CF) for all the studied metals of all samples are presented in **Table 3**. Based on the classification of the six categories of CF, water samples suffered severe contamination by all metals except Ni, and Zn. In this study, the surface water was highly polluted with Pb followed by Cd, Cr and Cu. Meanwhile, for the other two samples, soil and mosses, all the studied metals showed low to slightly contamination levels. In order to compare the pollution status of different places and conditions, pollution load index was calculated. It is an index that can be used to make a general conclusion of whether the studied stations were contaminated or not. Based on the results, all the studied samples have been polluted by the studied metals. The data of PLI as summarized in **Table 3** clearly shows that the surface water was mostly polluted by the metals followed by topsoil and moss.

Correlation analysis of metals

Correlation analysis is used in this study to statistically evaluate the strength of a relationship between all the studied metals and the possible relationship between them. The correlation between element pairs for all the studied metals in this study is summarized in **Table 4**. The Pearson correlation shows a positive correlation among all the studied metals except for the pairs of Cd-Cu, Cd-Ni, and Cd-Zn that were negatively correlated, meanwhile a weak correlation was recorded Cd-Cr pair and a relatively strong correlation for Cd-Pb. The correlations for the other pairs was recorded above 0.5 (strong correlation) which indirectly indicates that the existence of Cr, Cu, Ni, Pb, and Zn in the study area would probably be contributed by the same anthropogenic sources except for Cd.

Table 4 Pearson correlation analysis of heavy metals in the agricultural site

	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**
Cd	1					
Cr	0.02	1				
Cu	-0.18	0.98	1			
Ni	-0.46	0.88	0.96	1		
Pb	0.52	0.84	0.75	0.53	1	
Zn	-0.31	0.94	0.99	0.99	0.65	1

Conclusion

The results obtained in this study generally indicated that the concentrations of the studied metals were relatively high in topsoil and surface water but moderate to low in moss samples. Most of the measured metal concentrations were higher than the limits suggested by the WHO for specific applications. Contamination factor (CF), pollution load index (PLI), and correlation analysis indicated that the study area was polluted by the metals at certain levels. The results of in *situ* physicochemical measurements also suggested that the river water would be classified as Class III where the water needs to have extensive treatment prior to distribution to the consumers. It can be concluded that the surrounding environment of the study area was affected by the anthropogenic activities that indirectly related to the application of agrochemicals for agricultural activities. Therefore, in order to avoid the potential adverse effects on the local population, the related authorities should regulate appropriate agricultural rules and educate the farmers to reduce the use of insecticides and agrochemicals.

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Conflict of interests

Authors hereby declares that there is no conflict of interests with any organization or financial body for supporting this research.

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