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Determination of Heavy Metals and Polycyclic Aromatic Hydrocarbons (PAH) Contents Using the Lichen *Dirinaria picta* in Universiti Kebangsaan Malaysia

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ABSTRACT

A biomonitoring study on lichens was conducted to assess the levels of atmospheric heavy metal and polycyclic aromatic hydrocarbon (PAH) at ten sites at the Universiti Kebangsaan Malaysia Campus, Bangi, Selangor, Malaysia. *Dirinaria picta*, epiphytic lichen which commonly found at lowland areas was used as the bioindicator in this study where samples were collected from the bark of palm trees at sites ranging from areas with high volume of traffic to isolated areas in the campus. Eight metals (Cr, Fe, Co, Ni, Cu, Zn , Al, Pb), and ten PAH; naphthalene (PAH_1), acenaphtylene (PAH_2), acenaphthene (PAH_3), fluorine (PAH_4), anthracene (PAH_5), phenanthrene (PAH_6), fluoranthene (PAH_7), pyrene (PAH_8), benzo (b) anthracene (PAH_9) and chrysene (PAH_{10}) were analyzed in the naturally growing thallus of *Dirinaria picta.* The average concentration of the metals was observed to be in the range of 230.6 ppm (Fe) to 0.3 ppm (Co) and for PAH, it was observed in the range of 612 ppm (PAH_1) to 79.5 ppm (PAH_{10}). The One-way ANOVA analysis for both the heavy metals and the PAHs showed H_o was rejected. There are significant differences in heavy metals and PAHs concentrations between sites. The selectivity sequence of heavy metals were Fe > Cr > Ni > Al > Zn > Pb > Cu. Meanwhile for PAH, the sequence is $PAH_1 > PAH_3 > PAH_2 > PAH_6 > PAH_5 > PAH_7 > PAH_4 > PAH_8 > PAH_9 > PAH_{10}$.

Keywords: Air Quality; Bioindicator; Heavy Metals; PAH; *Dirinaria picta*

1. Introduction

The developmental efforts in Malaysia to become an industrialized nation by 2020 has had a significant effect on the quality of air that in turn negatively affects public health and her diverse ecosystem. The three major causes of air pollution are transportation, stationary sources and open burning [1]. The Department of Environment is the body that carries out air pollution control and monitoring as a means to offset the decreasing air quality in the nation [2,3]. The problem they face now is that the quality of air in areas far away from their air monitoring stations is difficult to determine, hence lichen has been selected as a potential bioindicator for this purpose.

Lichen is a very unique species which exists in a symbiotic relationship between fungus and algae. This species has no complex organs such as roots, leaves or bark [4]. The use of lichen as a potential bioindicator to measure the air quality has long been recognized since last few decades [5]. Their anatomy and morphology which has no waxy cuticle on the upper surface has made the accumulation of air particles with heavy metal and polycyclic aromatic hydrocarbon (PAHs) contents feasible.

Heavy metals and PAHs are common parameters that could be measured to determine the level of air quality. Heavy metals such as cadmium, lead and mercury are common air pollutants emitted as a result of various industrial activities and have been reported to have adverse effects on human health [6]. PAHs are semi-volatile organic compounds, distributed both in the vapor- and particle-phases of the air. The sources of these compounds are mainly from industrial activities and vehicles emissions [6]. Many researchers are interested to study about PAHs in atmosphere because of their mutagenic and car-

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cinogenic characteristic [7]. The simplest technique to determine both heavy metals and PAHs content is ICP-OES and gas chromatography respectively.

2. Experimental Design

2.1. Sampling

The samples of lichen *Dirinaria picta* were collected around UKM, Bangi at ten locations (**Figure 1**). Sites 1-6 are near the entrance of the University where traffic is busy along the public road, whilst sites 7, 8a and 8b are at the inner campus where the traffic are limited to vehicles used by UKM staff and students. Sites 9a, 9b and 10 are located at a quieter place where very few vehicles pass by. The lichens were cleaned, oven dried at 60˚C for 48 hours and ground for further analysis.

2.2. Heavy Metal Analysis

The ground samples then were homogenized. About 1 g of samples was weighted accurately for 3 replicates and digested using wet acid digestion procedure [8-10]. The acid mixture used for digestion is 5.0 mL nitric acid 65% and 2.0 mL hydrogen peroxide 30%. After that, the mixtures were heated on the hot plate at 90˚C for 4 hours. The residue of digestion then was rinsed ~~by~~ with 1 mL hydrochloric acid 2% and diluted to 100 by deionized water before carrying out the ICP-OES (Optima 4300 DV, Perkin Elmer) analysis.

2.3. Polycyclic Aromatic Hydrocarbon Analysis

Approximately, 2 g of ground sample was extracted in a Soxhlet apparatus with 250 mL dichloromethane (DCM) for 24 h gel column with 25 mL of DCM: pentane (2:3 v/v) as eluting solvent. The samples were again evaporated and concentrated with a gentle stream of purified nitrogen to 1 mL. Then, they were analyzed using Gas Chromatography/Mass Spectrometer (GC/MS) (Agilent 7890A coupled with Agilent 5975C MS system) by using

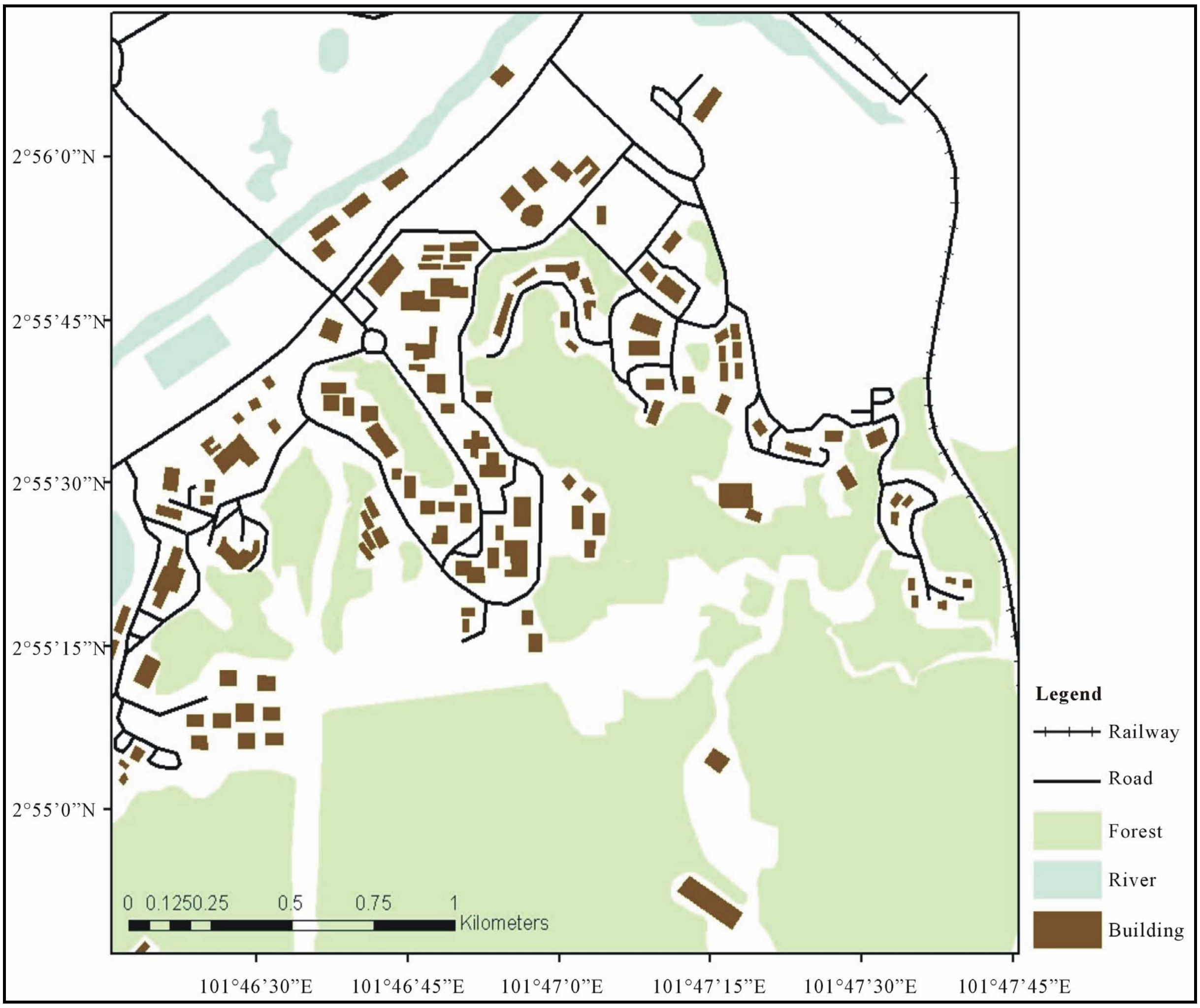

Figure 1. Sampling locations, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia.

AB-5MS capillary column. The identification of PAH compounds were carried out by both mass spectra and retention time compared to external PAH standard.

2.4. Statistical Analysis

One-way ANOVA is tested to evaluate the result of heavy metals and PAHs concentration. SNK Test was also performed to check significant comparisons between each of the heavy metals and PAHs.

3. Result and Discussion

In this study, the heavy metals found are Fe, Cr, Ni, Zn, Al, Pb and Co. Meanwhile, the PAHs found are napthalene (PAH_1), acenaphtylene (PAH_2), acenaphthene (PAH_3), fluorine (PAH_4), anthracene (PAH_5), phenanthrene (PAH_6), fluoranthene (PAH_7), pyrene (PAH_8), benzo (b) anthracene (PAH_9) and chrysene (PAH_{10}).

Tables 1 and **2** show the analysis of heavy metals and PAHs concentration. Based on **Table 1**, the average concentration of heavy metals was in the range between 0.316 ppm (Co) and 230.55 ppm (Fe). Almost all concentration of heavy metals at location 2 gave the highest reading except for metal Cu (Fe = 485.20 ± 3.21 ppm, Cr = 107.8 ± 3.75 ppm, Ni = 53.79 ± 2.34 ppm, Zn = 14.35 ± 2.76 ppm, Al = 29.38 ± 3.42 ppm, Pb = 2.758 ± 0.54 ppm and Co = 0.71 ± 0.23 ppm). For metal Cu, the highest reading was recorded at Location 3 (2.68 ± 1.05 ppm). Meanwhile, for PAHs analysis (**Table 2**), the average concentration was in the range between 27.62 ppm (PAH_{10}) and 177.13 ppm (PAH_1). Location 1 gave the highest concentration for almost of the PAHs except for PAH_6 and PAH_9. For PAH_6 and PAH_9, the highest reading was recorded at Location 3. The highest concentration reading for PAHs are; PAH_1 (612.80 ppm), PAH_2 (369.20 ppm), PAH_3 (395.30 ppm), PAH_4 (283.80 ppm), PAH_5 (189.90 ppm), PAH_6 (178.80 ppm), PAH_7 (290.30 ppm), PAH_8 (168.10 ppm), PAH_9 (120.90 ppm) and

Table 1. Heavy metal accumulation (ppm) in lichen *Dirinaria picta* at Universiti Kebangsaan Malaysia, Bangi, Selangor.

Heavy metals	Location 1	2	3	4	5	6
Cr	17.45 ± 0.26	107.8 ± 3.75	5.69 ± 1.31	62.88 ± 3.11	103.00 ± 4.65	7.343 ± 2.71
Fe	107.00 ± 3.15	485.2 ± 3.21	61.54 ± 2.94	296.9 ± 4.32	452.2 ± 10.32	85.95 ± 4.16
Co	0.11 ± 0.08	0.71 ± 0.23	0.047 ± 0.02	0.43 ± 0.13	0.6957 ± 0.16	0.0676 ± 0.013
Ni	7.94 ± 1.12	53.79 ± 2.34	2.15 ± 0.67	31.47 ± 3.51	52.07 ± 3.23	3.464 ± 0.96
Cu	1.43 ± 0.32	2.21 ± 0.88	2.68 ± 1.05	1.72 ± 0.56	1.967 ± 0.37	1.262 ± 0.83
Zn	20.75 ± 2.73	14.35 ± 2.76	8.92 ± 1.77	7.36 ± 1.18	10.8 ± 1.22	12.25 ± 1.34
Al	16.07 ± 1.67	29.38 ± 3.42	16.65 ± 3.02	21.70 ± 3.32	19.41 ± 2.59	21.93 ± 2.78
Pb	2.018 ± 0.64	2.758 ± 0.54	1.94 ± 0.61	2.291 ± 0.51	1.734 ± 0.46	1.817 ± 0.35
Total	172.77	696.2	99.62	424.75	641.88	134.08
One-way ANOVA						
F	2.16					

Heavy metals	Location 7	8a	9a	10	Average	F
Cr	21.91 ± 2.68	98.47 ± 4.54	7.315 ± 1.16	24.18 ± 2.74	45.60	17.28
Fe	146.4 ± 4.11	437.5 ± 5.89	75.19 ± 2.44	157.6 ± 4.76	230.55	
Co	0.1752 ± 0.045	0.6716 ± 0.28	0.0732 ± 0.02	0.1819 ± 0.03	0.32	
Ni	10.84 ± 1.95	50.87 ± 3.77	3.615 ± 0.54	12.09 ± 1.06	22.83	
Cu	1.352 ± 0.23	1.413 ± 0.29	1.029 ± 0.05	1.713 ± 0.085	1.68	
Zn	10.91 ± 1.38	12.11 ± 1.48	10.30 ± 1.09	11.09 ± 1.38	11.88	
Al	26.61 ± 2.27	24.27 ± 3.74	17.73 ± 2.13	23.75 ± 3.11	21.75	
Pb	1.987 ± 0.19	1.787 ± 0.32	1.306 ± 0.21	2.573 ± 0.96	2.02	
Total	220.18	627.09	116.56	233.18		
One-way ANOVA						
F	2.16					

Table 2. PAH accumulation (ppm) in lichen *Dirinaria picta* at Universiti Kebangsaan Malaysia, Bangi, Selangor.

PAHs	Location										Average	F
	1	2	3	4	5	6	7	8b	9b	10		
PAH_1	612.80	142.80	269.80	127.30	177.20	154.90	142.80	124.3	19.42	n.d.	177.13	6.29
PAH_2	369.20	110.20	140.80	111.10	64.20	20.45	21.99	6.98	7.26	n.d.	85.22	
PAH_3	395.30	189.20	139.30	44.92	61.14	20.07	11.89	7.78	5.63	6.89	88.21	
PAH_4	283.80	45.60	135.90	48.19	45.34	24.90	4.56	4.37	4.56	n.d.	59.72	
PAH_5	198.90	119.90	142.60	75.63	161.20	12.29	8.55	5.13	9.33	n.d.	73.35	
PAH_6	148.80	168.80	178.80	50.39	175.20	10.72	14.84	4.63	5.23	n.d.	75.74	
PAH_7	290.30	68.40	111.00	63.41	44.63	32.04	24.83	4.53	n.d.	n.d.	63.91	
PAH_8	168.10	52.38	86.21	35.25	33.65	30.06	21.49	n.d.	n.d.	n.d.	42.71	
PAH_9	103.00	44.06	120.90	42.07	33.39	4.76	16.46	n.d.	n.d.	n.d.	36.46	
PAH_{10}	79.50	42.85	56.42	28.73	41.21	13.01	14.45	n.d.	n.d.	n.d.	27.62	
Total	2649.70	984.19	1381.73	626.99	837.16	323.20	281.86	157.72	51.43	6.89		
One-way ANOVA												
F	1.99											

n.d.—not detected; naphthalene (PAH_1), acenaphtylene (PAH_2), acenaphthene (PAH_3), fluorine (PAH_4), anthracene (PAH_5), phenanthrene (PAH_6), fluoranthene (PAH_7), pyrene (PAH_8), benzo (b) anthracene (PAH_9) and chrysene (PAH_{10}).

PAH_{10} (79.50 ppm).

One-way ANOVA analysis for both heavy metals and PAHs shows there are significant differences between heavy metals and PAHs concentration and location (F = 2.16 and F = 1.99 respectively). The concentration of heavy metals and PAHs are different for every location. SNK Test for both analysis (**Tables 3** and **4**) shows there are significant comparison between each heavy metals and PAHs. Hence, the selectivity of heavy metals is Fe > Cr > Ni > Al > Zn > Pb > Cu > Co while for PAHs is $PAH_1 > PAH_3 > PAH_2 > PAH_6 > PAH_5 > PAH_7 > PAH_4 > PAH_8 > PAH_9 > PAH_{10}$.

The emissions of heavy metals are mostly from the combustion of automobile engines. According to Garty *et al*. [11], Pb is the main heavy metal which originates from tetraethyl lead in engine fuel. This compound was an additive prior to the usage of unleaded fuel nowadays. Besides Pb, almost all of the heavy metals pollutants were attributed to the vehicle transportation (*i.e.*: Cu from automobile engines' compartment, Al and Fe from the corrosion of vehicles' body). As for PAHs, the source of emissions is mainly from vehicles especially motorcycles [12,13].

In this study, it was discovered that the concentration of Fe and naphthalene (PAH_1) were the highest in concentration for all of the sample locations. Naphthalene is the lightest molecular weight of PAHs so that it is the most abundant PAHs in atmosphere [14]. For heavy metals analysis, it was found that the concentration values at Locations 2, 5 and 8a were quite high. Whilst for PAHs analysis, Locations 1, 2, 3 and 4 were found to

Table 3. SNK test for heavy metals analysis.

Comparison	q_{cal}	q_{tab} (0.01)	q_{tab} (0.05)	P Value
Fe-Co	10.23	5.52	4.32	8
Fe-Cu	10.07	5.13	4.16	7
Fe-Pb	9.83	4.76	3.94	6
Fe-Zn	9.34	4.02	3.23	5
Fe-Al	6.51	3.44	2.98	4
Cr-Co	10.12	5.11	3.94	7
Cr-Cu	9.32	4.72	3.63	6
Cr-Pb	9.66	4.39	3.08	5
Cr-Zn	8.82	3.90	2.85	4
Cr-Al	5.49	2.77	1.55	3
Ni-Co	9.21	4.97	3.36	6
Ni-Cu	8.74	4.63	2.98	5
Ni-Pb	8.05	4.04	2.47	4
Ni-Zn	7.68	3.62	2.04	3
Ni-Al	4.08	2.39	1.34	2

have higher concentration The higher concentrations may be due to high traffic near to these locations. The road along these locations is the main road from Bangi to Kajang. So, it is congested with many kinds of vehicle every day. Most of researchers reported that there is a positive relation between heavy metals/PAHs emissions and vehicles' traffic [15,16]. The rest of location gave an acceptable average concentration value in the range of 27.62 - 36.46 ppm. This is due to the low traffic flow along the road near these locations. Thus the concentra-

Table 4. SNK Test for PAHs analysis.

Comparison	q_{cal}	q_{tab} (0.01)	q_{tab} (0.05)	P Value
PAH_1-PAH_{10}	15.23	8.67	7.71	10
PAH_1-PAH_9	14.76	8.34	7.58	9
PAH_1-PAH_8	14.22	7.88	7.01	8
PAH_1-PAH_4	13.89	7.42	6.69	7
PAH_1-PAH_7	13.32	7.02	6.11	6
PAH_1-PAH_5	12.71	6.79	5.97	5
PAH_1-PAH_6	12.13	6.28	5.32	4
PAH_1-PAH_2	11.64	5.66	5.77	3
PAH_1-PAH_3	11.16	5.32	5.48	2
PAH_3-PAH_{10}	12.83	6.45	4.36	9
PAH_3-PAH_9	12.27	6.08	3.99	8
PAH_3-PAH_8	11.65	5.65	3.25	7
PAH_3-PAH_4	11.29	5.27	2.82	6
PAH_2-PAH_4	10.73	4.87	2.24	5
PAH_2-PAH_7	10.02	4.33	1.77	4
PAH_2-PAH_5	9.69	3.78	1.32	3
PAH_2-PAH_6	9.07	3.32	1.01	2

tions of heavy metals and PAHs in lichens at the UKM campus clearly correspond to the exposure of the lichens, particularly *Dirinaria picta*, to source of vehicular emissions.

4. Conclusion

By this study, it is proven that *Dirinaria picta* acts as a good bioindicator in monitoring and determining the level of air quality. The main factor attributed is its ability to accumulate the air particles which contain heavy metals and PAHs. Both ICP-OES and GC/MS techniques were effective in determining heavy metals and PAHs respectively. In future, it is recommended to use transplanted lichen in order to see the trend of air pollutant in interested research area.

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