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APPLICATION OF MOSS AS BIO-MONITOR FOR HEAVY METALS DEPOSITION IN PORT DICKSON, MALAYSIA

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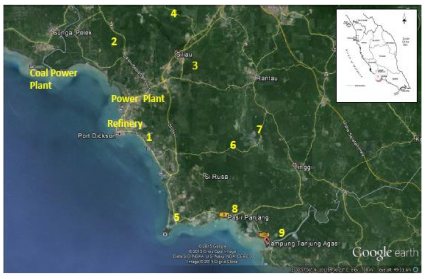
Graphical abstract



Abstract

Port Dickson in Malaysia is a sea-side township of mixed activities within the area, comprising of a coal-fired power plant, a petroleum refinery, a gas-fuelled power plant, and tourism with the visit of many road vehicles, especially during weekends and public holidays. The impact of emission from these activities to the environment has becomes a matter of concern to the authorities as well as local residents. The present study embarked on the use of mosses (*Octoblepharum* sp. & *Isopterygium* sp.) as long terms monitor of heavy metals emission from such activities. Mosses samples were collected on land area within 30 km radius from the town centre. Prepared samples were analysed for the concentration of As, U, Th, Fe, Cr and Zn using Neutron Activation Analysis (NAA) technique. These metals are related to various industries, fuel combustion and refineries emissions. Although the results show no elevated concentration of the elements studied, except for Cr, the spatial pattern of heavy metal distributions observed reflected the energy-related activities and vehicular emissions in the study area. Enrichment Factor values of each element also in agreement with the distribution pattern. The research finding suggests that 'moss-method' is applicable for deposition measurement in vicinity of stationary as well as non-point sources.

Keywords: Bio-monitor, heavy metals deposition, enrichment factor, moss

1.0 INTRODUCTION

A small sea-side tourism township like Port Dickson in Malaysia, with mixed activities is prone to air pollution as the consequences of anthropogenic emission. The close proximity of energy generation and petroleum refinery to the residential areas, coupled with vehicular emissions had raised interest on the extent of such pollution to human health. Studies indicated that increasing exposure to toxic elements in terrestrial as well as marine organisms would generate adverse toxicological consequences (Rana et al., 2004; Katranitsas, *et al.*, 2003).

Earlier study on airborne particulates matter collected in an area around a coal-fired power-plant showed an appreciable presence of elements such as Cr, Cu, Zn, Hg, Fe, As, Se, Pb, U and Th and Cd (Nursyairah Arshad *et al*., 2015). While results of a study on mosses collected around a gas and petroleum-related industrial area detected the presence of V, Mn, Cu, Cr, Zn, Hg, Pb, As, Se, Th, and U, the concentration of which very much dependence on

the distance from the industrial area, and the wind direction (Mohd Zahari *et al*., 2012). This is not surprising as metals and organo-metallic species are incorporated during petroleum refining processes. Duyck *et al*. (2007) reported that toxic elements such as Zn, Cr, Ni, V, Cd, Cu and Pb can be sourced to crude oil, which consequently be related to petroleum refinery. Another study also reported higher concentrations of toxic elements such as Cr, Mn, Ni, Rb, Cs, La and Sm the oil refinery and petrochemical industry complex (Anicic *et al*. 2007). The enrichment of Cd and Zn in moss samples collected in a tourism area in Malaysia traced the sources of Cd in air to incineration of solid waste, fossil fuel burning and application of phosphate fertilizer, while Zn can be attributed to ware of tires and incomplete fossil fuel burning (Ahmad *et al*., 2014).

The estimation of atmospheric heavy metal depositions by using bryophytes (mosses) as bio-monitors has been widely used for the last three decades. The moss monitoring technique, first introduced in Scandinavia, has shown to be very suitable for studying atmospheric deposition of heavy metals and other elements as well (Ruhling *et al*. 1987; Harald, 2004; Anicic *et al*. 2007). More recently, bio-monitoring technique using lower plants such as lichen and moss to assess the impact of heavy metals pollutants is popular in many countries like Serbia (Dragovic & Mihailovic, 2009), Turkey (Ugur *et al*., 2003), Italy (Pellegrini *et al*., 2014), Seri Lanka (Pemasinghe and Deeyamulls, 2009), Romania (Lucaciu *et al*., 2004), and even in Antartica (Zverina *et al*., 2012). Mosses are suitable for such monitoring since they are resistant to many substances at higher concentration which are toxic to other plants. Mosses being lack of root system accumulate water and nutrients largely through the atmosphere (Ugur *et al*., 2003). Being Bryophyte the leaves of mosses are lack of protective cuticle, hence accommodate mineral nutrition accumulation mainly from wet and dry deposition (Anja *et al*., 2004). The uptake mechanism of lichens and mosses tends to accumulate pollutant as well.

Using natural bio-monitors for monitoring atmospheric quality in both urban and rural environments could minimise and avoid detrimental effects of toxic metals on the researchers (Szczepaniak and Biziuk, 2003; Bargagli *et al*., 2002). Thus, this study explore the applicability of moss species to investigate the presence and distribution of As, U, Th, Zn, Cr, and Fe in the vicinity of the study area. Assessment of anthropogenic input based on enrichment of each element in samples was also carried out.

2.0 EXPERIMENTAL

2.1 Sampling and Sample Preparation

Based on their availability, moss samples *Octoblepharum sp.* and *Isopterygium sp.* were collected from nine different locations within 30 km distance from the town centre of Port Dickson, Negeri Sembilan on the west coast of Peninsular Malaysia. The town is annually exposed to the Southwest Monsoon wind. At each location samples were collected during relatively dry months from May to August from several trees trunks at a height of between 0.5 and 2 m above ground level. Figure 1 shows the sampling locations relative to the town centre, a petroleum refinery, a coal-fired power plant and a power generation plant. While Table 1 shows details of the sampling locations, including distance from the town centre.

Figure1 Sampling points relative to locations of refinery and power plants. The inserted map of Peninsular Malaysia shows location of Port Dickson

Table 1 Sampling Details

Site no.	Location Code	Dist. (km)	GPS
1	TDI	5	N 02° 30.920' E 101° 50.366'
2	TM	8	N 02° 37.566' E 101° 48.246'
3	LS	11	N 02° 35.168' E 101° 52.189'
4	KJL	13	N 02° 39.248' E 101° 50.952'
5	THM	14	N 02° 25.503' E 101° 52.654'
6	AKR	15	N 02° 30.202' E 101° 56.517'
7	AK	18	N 02° 32.440' E 101° 58.576'
8	PP	20	N 02° 25' 51.95' E 101° 56' 16.54'
9	TA	25	N 02° 23' 35.620' E 101° 58' 36.514'

The unwashed samples were cleaned from extraneous plant material and were oven dried for 48 hours at 60°C, until a constant weight. The unwashed approach was adopted since many large-scale monitoring projects on atmospheric deposition are commonly based on the total element analysis of unwashed moss samples (Ruhling *et al*., 1987; Steinnes,

1994; Sucharova and Suchara, 2004). Samples then were ground into powder form using an agate bowl ball-mill grinding machine and sieved using 250 µm stainless steel sieve.

2.2 Irradiation and Counting

Samples were prepared in two replicated. About 0.3 g of each samples and standard references materials (SRM) (Lichen 336 IAEA (International Atomic Energy Agency) and SRM- 1575 (pine needles) from the US NIST (National Institute of Standards and Technology) were heat-sealed in polyethylene irradiation vials.

By applying Neutron Activation Analysis (NAA) technique, samples and SRM were irradiated together in the rotary rack (RR) facility of the TRIGA Mark II reactor at the Malaysian Nuclear Agency. The normal operating power of the reactor is 750 KW with a thermal flux of about 10^{12} cm^{-2} s^{-2}. Irradiated samples were counted using an HPGe detector with a relative efficiency of 30 % and resolution of 1.8 KeV (FWHM) at 1.33 MeV. The photo peaks analyses were performed by using Apex software (Canberra Inc). Irradiation, cooling and counting times were optimized in order to determine long-lived and medium-lived radionuclides. After a 6 hours irradiation time and a cooling period of 3 days, the irradiated samples were counted for 3600s to evaluate the medium half-life radionuclides. And, after 3 weeks the same samples were counted for 7200 s to determine the concentration of long half-life radionuclides.

3.0 RESULTS AND DISCUSSION

The interested elements (As, Cr, Zn, Fe, Th and U) concentrations (mg/kg) were determined by using comparison method between the corrected gamma-peak area of the samples to the corresponding peak area of the Standard Reference Materials. In the calculations dead-time corrections were also carried out. The mean elemental concentrations of replicated measurements in mosses sample are summarized in Figure 2. To evaluate the spatial distributions of each element, iso-maps of each element were constructed based on the mean concentration at each location. Figure 3 shows the distribution pattern of each element in the study area. In the figure only the minutes scale of the latitudes and longitudes are shown. The relative position of the Port Dickson town is also shown.

Depending on sampling locations, the concentrations of As, Cr, Zn, Fe, Th and U in the studied locations were found to be in the range of 1.1 mg/kg to 20.5 mg/kg, 3.7 mg/kg to 29.2 mg/kg, 12.9 mg/kg to 70.7 mg/kg, 13.2 mg/kg to 139.1 mg/kg, 1.78 mg/kg to 22.9 mg/kg and 0.5 mg/kg to 4.0 mg/kg respectively. The results show that heavy metal concentrations observed somewhat reflected the proximity of the locations to the various energy-related activities around the Port Dickson town area. These toxic elements were perhaps released to the atmosphere during such combined activities, and being adsorbed to and absorbed by the moss samples. A very distinct observation at KJL is that all elements show lowest concentrations while highest concentration of Fe is at TM, Zn at THM, and Cr at LS. Being furthest from the refinery and both power generation plants the concentrations at TA are relatively low, except for combustion related element Zn, and Fe. This finding is in agreement with Zahari *et al*. (2012) that reported elevated concentrations of Cr, Fe and Zn can be related to the oil refinery industry.

The tolerable level of as for plant growth is 20 mg/kg (Adamu & Nganje (2010). Except for samples collected from TM, about 8 km from town centre, all sample show as concentration of lower than 20 mg/kg. Although as is normally related to petrochemical industries (Zahari *et al*., 2012), the present study indicated that these activities do not contributed to deposition of As in the study area. The baseline level for Cr in unpolluted regions is lowers than 0.3 mg/kg (Ruhling *et al*., 1987). The main source of Cr is iron and steel mills, however Anicic *et al*. (2007) and Mohd Zahari *et al* (2012) reported that Cr were also found around refinery and petroleum related industries. The present results show that the concentration of Cr at all locations exceeded 0.3 mg/kg indicating accumulation of Cr in the moss samples.

For Zn, samples from all locations show very much lower concentration than the tolerable level for plants, that is 300 mg/kg (Adamu & Nganje, 2010). Although Zn could be originated from multiple sources this observation is quite similar to the earlier study by Mohd Zahari (2012), around a petro-chemical industrial area in Malaysia that show an average of 43.1 mg/kg. Besides, Zn could also be attributed to dust and fumes released from refuse incinerator (ATSDR, 2015). Earlier studies showed that the content of Fe in mosses from unpolluted areas is generally lower than 500 mg/kg (Ruhling *et al*., 1987). Fe is considered lithogenic element. Although majority of the samples show relatively higher concentration of Fe than other elements, however not a single location registered the Fe concentration that exceed the unpolluted areas value of 500 mg/kg.

Th and U concentrations are highest in samples collected from TM, which are much higher than the world average concentration of 7.4 mg/kg for Th and 2.8 mg/kg for U (UNSCEAR, 2000). This not surprising since TM is relatively closer to the coal-fired power plant, the refinery and the gas-fueled power plant compared to other sampling locations. The results of the present study quite in agreement with of Zahari (2012) with the average concentration of 6.3 mg/kg and 4.2 mg/kg respectively for Th and U.

To have some insight into the spatial distributions of the studied elements within the boundary of the study area, we could observe the iso-maps of the elements in Figure 3. The maps for As, Fe, Th and U show somewhat similar pattern of higher distribution on the north-west and south-east regions of the study area. The north-west region being nearest to the both power

plants and the refinery shows the highest distribution of concentrations for such elements.

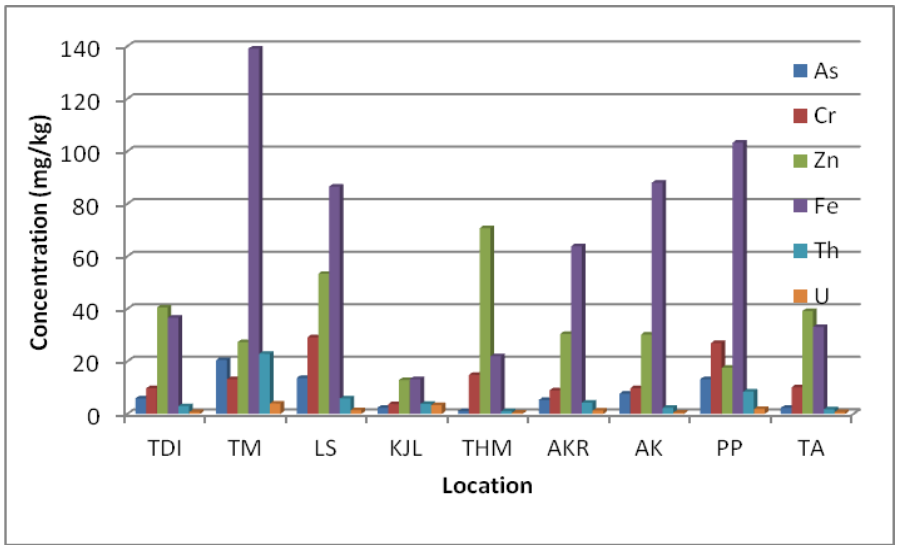


Figure 2 Concentration (mg/kg) of toxic elements in mosses sample

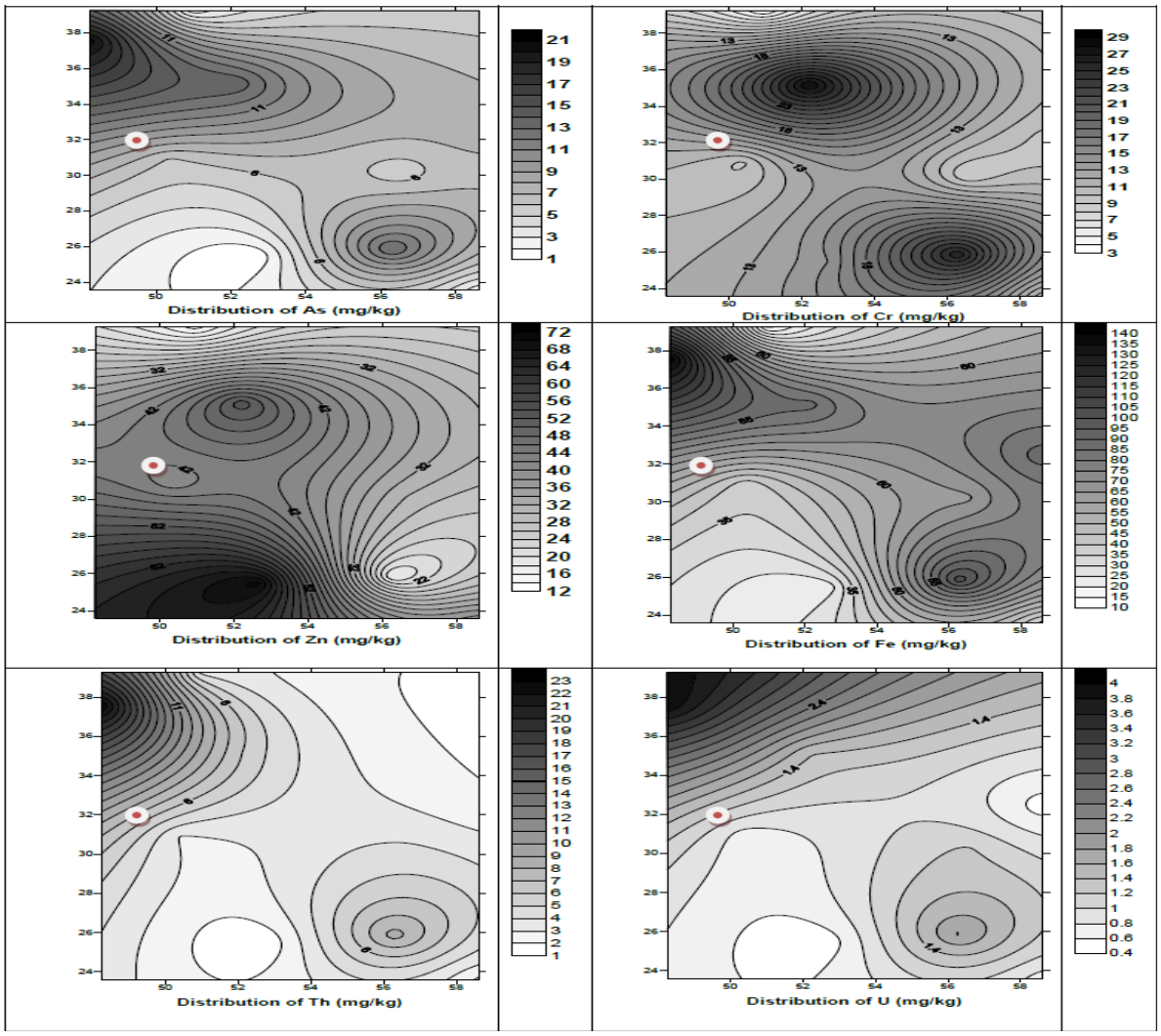


Figure 3 Distribution of heavy metals concentration (mg/kg) in moss samples. The dot shows the location of Port Dickson town

The pattern for Cr shows higher distribution on the central north and south-east regions, indicating other unknown sources, on top of the combined effect from refinery, power plants as well as vehicular emissions. However, Zn shows very high distribution in the central south region. This region is located near the sea-side tourist attraction spots, where thousands of visitors flocked especially during weekends and public holidays. Hence Zn could be attributed to the vehicular emissions from combustion of fossil fuel (Arditsoglou and Samara, 2005; Pacyna and Pacyna, 2001; Pellegrini, 2014; Anicic *et al*. 2007).

Although not emphasized in this study, it is worth mentioning that the distributions of such elements over the area depend also on the average wind direction and speed, as well as the chemical state of such elements (Pemasinghe and Deeyamulls, 2009; Mohd Zahari *et al*., 2012; Nursyairah Arshad *et al*., 2015). The chemical state would be related to the size of air particulate matter it will be attached to. While the sizes of particulate matter determines how far it will be blown from its sources.

A correlational study between the elements based on Pearson's Correlation factor was also carried out to check the commonness of sources, as shown in Table 2. Just like the observation on the distribution pattern as described earlier, relatively high correlation exists between As, Fe, Th and U, while Cr and Zn either weakly correlated or not correlated to other elements. This somehow enhance the prediction that As, Fe, Th and U originated from the same sources, related to the combined energy-related activities in the study area. Whereas Zn and Cr could be attributed to other non-point sources.

Table 2 Pearson's Correlation factor between elements

	As	Cr	Zn	Fe	Th	U
As	1	0.54	-0.24	0.94	0.87	0.55
Cr		1	0.26	0.49	0.19	-0.07
Zn			1	-0.27	-0.32	-0.58
Fe				1	0.79	0.39
Th					1	0.78
U						1

Finally the degree of elemental enrichment in the samples was calculated using Enrichment Factor (EF). This factor could be used to evaluate the anthropogenic input or influences of the elements in the moss samples. The EF was calculated using the approach used by Sakan *et al*. (2015). In this calculation, samples from TA, which is a remote location, furthest from the town centre was assumed as the control site, while Fe was used as the element for normalization. The EF values were evaluated for enrichment as follows: EF<1, nil; EF<3, minor; 3<EF<5, moderate; 5<EF<10, moderately severe; and >10, severe.

Table 3 Enrichment Factors of elements in samples from various sampling locations

	As	Cr	Zn	Fe	Th	U
TDI	2.8	1.1	1.1	1.2	1.8	1.1
TM	37.4	5.4	2.9	17.6	54.0	24.2
LS	15.6	7.5	3.6	6.8	8.5	5.4
KJL	0.4	0.1	0.1	0.2	0.9	1.9
THM	0.3	1.0	1.2	0.4	0.4	0.5
AKR	4.4	1.7	1.5	3.7	4.6	3.4
AK	8.9	2.6	2.1	7.1	3.4	1.9
PP	17.9	8.3	1.4	9.7	14.9	8.3

Relative to the remote sampling location TA, Table 3 shows severe enrichment of As, Fe, Th and U at TM, while at PP the same elements show moderately severe to severe levels of enrichment. This observation is consistent with the distribution pattern of Figure 3. KJL, THM and TDI are locations that show moderate enrichment or lower for all elements in moss samples. Although relatively higher concentration of Zn and Cr was observed in moss samples, however based on the EF values, most study locations show that these elements fall under the categories of no enrichment or minor enrichment.

4.0 CONCLUSION

The study has shown that moss samples *Octoblepharum sp.* and *Isopterygium sp.* could be applied as bio-monitor for supplement and complimentary tools for long term accumulation of various heavy metals deposited by various energy-related activities as well as vehicular fuel combustion emissions. The study found that except for Cr, no elevated concentrations of As, Zn, Fe, Th and U was indicated in the moss samples. On the spatial distribution, As, Fe, Th and U displayed almost similar distribution pattern, however Zn and Cr distributions are disparate and unique for them only. With the consideration of the two operational power plants and an oil refinery in this area, it is believe that these activities are the major contributor of the heavy metals deposition in Port Dickson area however contributions from not-point sources such as vehicular emissions cannot be underestimated.

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