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ATMOSPHERIC DEPOSITION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHS) AROUND TWO METROPOLITAN AREAS IN SRI LANKA USING MOSS AS A BIOMONITOR

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ABSTRACT

Concentration of Polycyclic Aromatic Hydrocarbons (PAHs) in moss species *Hyophila involuta* in two metropolitan areas; Sapugaskanda oil refinery and Kelanitissa power plant were compared with baseline concentrations of PAHs in the moss collected from Sinharaja rainforest. Monthly sampling was done throughout a year from March 2013 to February 2014 and concentration of 16 PAHs was analysed by High Performance Liquid Chromatography (HPLC). The background level concentration of PAHs in moss is not at detectable or quantification levels and the total PAH concentrations in the Sapugaskanda oil refinery were in the range of 247–4,062 mg kg^{-1} whereas Kelanitissa power plant were 522–1,195 mg kg^{-1} by weight basis. The percentages of atmospheric deposition of low molecular weight (2 or 3 fused rings) PAHs in moss was significantly higher than high molecular weight (more than 3 fused rings) PAHs in moss around both sampling locations. Benzo(a)pyrene (BaP), which is the indicator of carcinogenicity was detectable in the Sapugaskanda oil refinery and the Kelanitissa power plant with an average of 2.6 (±1.9) and 2.1 (±1.0) mg kg^{-1} respectively.

KEY WORDS: Moss, PAHs, Air pollution, Biomonitoring, Sri Lanka

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) group of compounds which contains at least two or more fused aromatic rings and releases to the atmosphere by increasing of incomplete combustion of fossil or non-fossil fuels during the pyrolysis or pyrosynthesis processes (Maliszewska-Kordybach, 1999). Most of PAHs with low vapour pressure in the air are found in both gaseous and particle phase and light molecular weight PAHs (LMW PAHs) that have two or three aromatic rings are emitted in the gaseous phase, while high molecular weight PAHs (HMW PAHs) with five or more rings are emitted in the particulate phase (Lee *et al.,* 2010; Marr *et al.,* 2006).

Most of PAHs are toxic, mutagenic, carcinogenic and ability to accumulate for a long time in ambient air has become a serious health risk for humans (Abdel-Shafy *et al.,* 2016). United states environmental protection agency (USEPA) has classified 16 of PAHs as priority pollutants based on their carcinogenic and mutagenic properties such as Naphthalene(NAP), Acenaphthene (ACE), Acenaphthylene (ACY), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLA), Pyrene (PYR), Chrysene (CHR), Benz(a)anthracene (BaA), Benzo(k) fluoranthene (BkF), Benzo (b) fluoranthene (BbF), Benzo(a)pyrene (BaP), Dibenz(ah)anthracene (DahA), Indeno(1,2,3-c,d) pyrene (IcdP), Benzo(g,h,i) perylene (BaghiP) and BaP has been directly linked to lung cancer through its selective formation of adducts along a tumor suppressor gene and is the main indicator of carcinogenic PAHs (Bostrom *et al.,* 2002). Therefore concentration, source identification and transformation of PAHs in the atmosphere is important to control the level of PAHs pollution by introducing PAH emission regulations.

Biomonitoring is a cost-effective air monitoring method widely used and naturally occurring

vegetations namely mosses, lichens and pine needles are most frequently used as bioindicator to monitor the PAHs pollution (Wegener *et al.,* 1992; Oishi, 2013). Use of moss for biomonitoring survey was carried out using mosses in Scandinavia to monitor the atmospheric deposition of trace elements at the end of the 1960s (Rühling, 1968). The European Heavy Metals in Mosses Surveys (UNECE-ICP Vegetation) is a programme performed every 5 years since 1990 in European countries (Rühling, 2002). In 2010, the ICP Vegetation programme monitoring manual has been applied for POPs including PAHs in mosses as a pilot survey and introduced for the expanded moss survey in 2015. Even though the ICP Vegetation programme has recommended the sampling manual to analyze POPs including PAHs in 2015, most of the research work has been carried out using own procedures for PAHs analysis after following the sampling according to the ICP Vegetation manual established for heavy metals.

The levels of atmospheric deposition of PAHs in Sri Lanka has not been recorded yet. Therefore this study was done to (i) assess monthly and annual PAH atmospheric deposition using moss *Hyophila involuta* around two metropoltain areas in Sri Lanka; Sapugaskanda oil refinery and Kelanitissa power plant (ii) compare the biomonitoring measurements of PAHs in the selected metropolitan areas with the Sinharaja rain forest area which was selected as the remote area.

MATERIALS AND METHODS

Sampling

Moss species *Hyophila involuta* was collected near to the Sapugaskanda oil refinery (6° 57' 48.24" N, 79° 57' 27.36" E) and the Kelanitissa power station (6° 57' 83" N, 79° 52' 44" E) in the western province of Sri Lanka monthly from March 2013 to February 2014 and compared with the moss collected from Sinharaja rain forest area (6°21' N to 6°26' N, 80°21' E to 80°34' E) where the anthropogenic sources are minimum. Sampling sites were located about 300 m from the anthropogenic sources and any main road.

Sapugaskanda is considered as the largest industrial area in Sri Lanka because of the petroleum refinery (6°57'48.24" N, 79°57'27.36" E), three power plants namely the 160 MW CEB diesel power station (6°57'42.483 N, 79°57'36.36" E), the 51 MW Asia power station (6°57'54" N, 79° 57'28" E) and the 22 MW Lak Danavi power station (6°57'29" N, 79°572053 E). Further, there are several industries located in this area, mainly the Lanka industrial estates (Lindel) which is located in Sapugaskanda on 125 acres of land, and 19 other industries. The Lindel industrial estate, the petroleum refinery located outside the Lindel and the three power plants contribute to the total air pollution load in this area.

Kelanitissa power plant is a diesel fuel and naphtha-fired combined cycle power station, and is capable of producing nearly 500 MW of power. Transport network in this area is higher with the huge road traffic and the density of large vehicles are also higher because of the main assess road to port of Colombo is lies on this area.

Sample Preparation

The green and green-brown parts of moss species were washed two times to remove dust particles and dried to a constant weight at 40 ºC. Dried moss sample (5.00 g) was homogenized with anhydrous Na_2SO_4 (5 g) and transferred to a round bottom flask and extracted using 1:1 mixture of hexane: acetone (2 × 50 cm^3) for 30 min at 50 ºC. The volume of extracts was reduced and transferred into hexane using a rotary evaporator. The volume was further reduced to 1 cm^3 by a gentle flow of N_2 stream. The samples were cleaned on a silica column using dichloromethane as the mobile phase. The column was packed with silica gel (1.5 g) and anhydrous Na_2SO_4 (0.30 g) was added onto the top of silica gel. The column was pre-washed with dichloromethane (20 cm^3) and the moss sample extract (dissolved in 2 cm^3 dichloromethane) was introduced to the column and there after 5.0 cm^3 fractions were collected. The absorbance of the fractions was measured at 254 nm using UV-visible spectrometer (AquaMate 8000). First UV active fractions were collected and evaporated using a rotary evaporator. The residue was dissolved in acetonitrile (10 cm^3) and the volume was further reduced to 1.0 cm^3 by a gentle flow of N_2 stream. The sample was filtered through a 0.45 µm millipore membrane.

Analysis of PAHs

The recovered PAHs were analyzed by the HPLC system (Agilent 1200 Series) with two detectors; DAD (Agilent 1200 Series) with the wavelength set to 254 nm and FLD (Agilent 1100 Series) with wavelengths set at 250 nm (excitation) and 410 nm/ 460 nm (emission) and Vydac C18 column (length

250 mm, internal diameter 4.6 mm and particle size 5 µm). An eluent mixed with acetonitrile and water was used as the mobile phase. A gradient method that initiated from 55:45 of acetonitrile and water was applied. The proportion of water to acetonitrile was gradually increased up to 100:0 by a binary pump (Agilent 1200 Series). A gradient elution time programme was applied with the flow rate of 0.500 cm^3 min^{-1} for 30 min and the time programme used for PAHs analysis was acetonitrile to water ratio of 55:45 for 3.00 mins, gradually increased from 55: 45 to 100:0 from 3 min to 9 min and kept at 100% acetonitrile from 9 min to 30 min. The 16 US EPA priority PAHs were determined. The PAH mix standard containing the 16 PAHs (Supelco) was used for calibration.

Quality Assurance and Statistical Analysis

For each sample, spiked sample was used to identify the peaks and analyzed as duplicates. Statistical analysis was performed using the statistical software; Minitab17, USA.

RESULTS AND DISCUSSION

Total detectable PAHs in moss (mg kg^{-1}) were determined on dry weight basis. Detectable LMW PAHs (up to 3 rings) and HMW PAHs (more than 3 rings) were analysed by HPLC using DAD (λ; 254 nm) and FLD ($\lambda_{excitation}$; 260 nm $6 \geq \lambda_{emission}$; 410 nm) respectively. The chromatograms obtained for the moss collected from background sampling location; Sinharaja rainforest indicated that PAHs in moss were not at detectable or quantifiable levels. Detectable PAHs in moss collected from the Sapugaskanda oil refinery and Kelanitissa power plant are summarized for twelve months and the ranges of the detectable PAHs are given in Table 1.

The range of total PAHs in moss *Hyophila involuta* around Sapugaskanda oil refinery and Kelanissa power plant were 247-4,062 and 522-1,195 mg kg^{-1} respectively. The higher values were given only the months May and September.

Total PAHs in moss *Pseudoscleropodium purum* in Galicia, NW Spain and *Hypnum cupressiforme* in Basovizza, Italy showed 220–3,466 mg kg^{-1} and 164–2,871 mg kg^{-1} respectively by the industrial emissions (Ares *et al.*, 2009; Skert, 2010). The accumulation of PAHs in moss *Tillandsia recurvata* at Mezquital Valley, Mexico which is around petroleum refinery, industrial and residential combustion of fuel, waste incineration has been recorded as 143–2,568 mg kg^{-1} (Zambrano, 2009). The accumulation of PAHs in *Hylocomiums plendens* due to the huge traffic in Warsaw, Poland has been recorded as 828–3,573 mg kg^{-1} (Orlinski, 2002)

According to the monthly results obtained from HPLC, 15 PAHs analyzed were at detectable levels and 14 PAHs except IcdP were at quantification levels. PAHs were analysed for twelve months,

Table 1. Ranges of detectable PAHs (mg kg^{-1}) in moss collected two metropolitan areas (March 2013–February 2014).

#	PAH	Range of PAHs (mg kg^{-1})	
		Sapugaskanda oil refinery	Kelanitissa power plant
1	NAP	40.2–453.7	85.2–553.3
3	ACE	175.7–3,320.4	346.6–913.6
4	FLU	BQL–9.8	0.6–12.9
5	PHE	6.0–121.5	6.3–41.8
6	ANT	2.3–49.6	2.1–11.5
7	FTH	BQL–58.1	2.7–35.0
8	PYR	3.0–29.6	3.5–17.2
9	BaA	BQL–9.5	BQL–5.6
10	CHR	BDL–9.5	BDL–7.8
11	BbF	BDL–5.1	BDL–7.2
12	BkF	BQL–8.8	BQL–4.0
13	BaP	1.0–7.1	1.0–4.5
14	DahA	BQL–39.6	BQL–28.9
15	BghiP	BQL–22.6	3.2–8.1
16	IcdP	BQL	BQL
	ΣPAHs	246.9–4,062.4	521.5–1,195.3

BQL- Below the quantification level.
BDL- Below the detectable level.

HMW PAHs i.e. CHR, BkF, DahA and BghiP were not detected in certain months particularly June, July and August. May and September showed higher accumulation of PAHs than the other months around Sapugaskanda oil refinery. Concentrations of NAP, ACE were higher than other PAHs around the studied areas and the average concentrations of PAHs (mg kg^{-1}) in moss are shown in Figure 1.

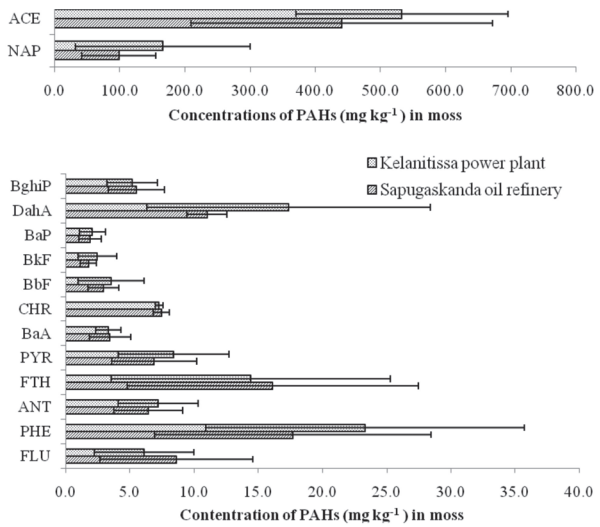

Fig. 1. Detectable concentration of PAHs (mg kg^{-1}) in moss around the Sapugaskanda oil refinery and the Kelanitissa power plant.

According to Figure 1, DahA showed higher accumulation in moss among HMW PAHs but DahA was detected only three months; October, November and February. Among the HMW PAHs, BaP (5-rings) which is the indicator of carcinogenicity was detectable throughout the year around the Sapugaskanda oil refinery and the Kelanitissa power plant with an average of 2.6 (±1.9) and 2.1 (±1.0) mg kg^{-1} respectively. Tire particles can contribute significant quantities of PAHs to street dust and (PHE, PYR, BghiP, IcdP, DahA) and BaP are the most dominant PAHs (>90% of total) in tire powder (Chen *et al.,* 2007). 80–90% of PAHs emitted from biomass burning are LMW PAHs, NAP, ACY, FLA, PHE and PYR (Lee *et al.,* 2010). Contribution of PAHs to two metropolitan area by different ring classes were compared using median based Mann-Whitney test ($p < 0.05$) and summarized in Table 2 for two sampling locations.

According to the data analyzed for different ring classes indicated there was not significant different for the accumulation of PAHs in Sapugaskanda oil refinery and Kelanitissa power plant areas even though three ring PAHs in moss around Sapugaskanda oil refinery are showed higher range than Kelanitissa power plant due to the higher accumulation of PAHs in the months May and September.

Further percentage of LMW PAHs in moss did not show significant difference between the two sampling sites (ANOVA, $p < 0.05$) and percentages of detected LMW PAHs in moss was higher than HMW PAHs in moss around both sampling locations. Therefore, percentage of LMW PAHs and HMW PAHs in moss around the two metropolitan areas are 94.7 (±2.6) % and 5.3 (±2.6) % respectively. The concentrations of LMW PAHs in moss *Hypnum cupressiforme* was higher than HMW PAHs in Hungary and the amount of HMW PAHs was less than 1% of by total concentrations of PAHs (Otvos *et al.,* 2004).

The PAH diagnostic ratios method for PAH source identification involves comparing ratios of pairs of frequently found PAH emissions and the ratio of these PAHs has been introduced to distinguish between traffic dominated PAH profiles and other sources (Gschwend *et al.,* 1981). In

Table 2. Detectable concentrations of PAHs (ng kg^{-1}) with different ring classes in moss in two metropolitan areas

	Sampling site	Range	Median
ΣTotal PAHs (mg kg^{-1})	Sapugaskanda	246.9–4,062.4	583.0 [a*]
	Kelanitissa	558.0–1,574.0	684.0 [a]
Σ3-ring PAHs (mg kg^{-1})	Sapugaskanda	186.5–3499.5	468.0 [a]
	Kelanitissa	390.7–969.4	533.7 [a]
Σ4-ring PAHs (mg kg^{-1})	Sapugaskanda	3.0–58.6	29.8 [a]
	Kelanitissa	7.2–52.6	29.0 [a]
Σ5-ring PAHs (mg kg^{-1})	Sapugaskanda	1.0–20.1	4.9 [a]
	Kelanitissa	1.1–39.6	5.9 [a]
Σ6-ring PAHs (mg kg^{-1})	Sapugaskanda	4.1–8.1	4.4 [a]
	Kelanitissa	3.2–8.1	4.4 [a]

addition to identifying traffic dominated PAH profiles, various diagnostic ratios such as PHE/ANT, FLA/PYR, PHE/PHE+ANT, FLA/FLA+PHY, IcdP/IcdP+BghiP and BaA/BaA+CHR have been applied in many studies to identify emission sources of PAHs (Yunker *et al.,* 2002; Dolegowska *et al.,* 2011). If ratio of BaA/BaA+CHR was higher than 0.35 indicated the car traffic emissions while the coal and wood combustion showed less than 0.35 (Yunker *et al.,* 2002). Another diagnostic ratio (three+four ring/total PAHs) has been used and reported that a ratio higher than 0.9 indicates wood combustion sources, whereas about 0.7 points to coal combustion sources (Migaszewski, 2009). The ratio obtained for BaA/BaA+CHR and from this study was 0.30 (0.09) and 0.27 (0.07) for Sapugaskanda oil refinery and Kelanitissa power plant respectively even though the areas are highly polluted by petroleum related activities. The ratio of three+four ring/total PAHs also higher than 0.9 around both areas. Further use of diagnostic ratios method should be used with caution as it is difficult to discriminate among various sources (Ravindra *et al.,* 2006).

Biomonitoring results obtained from moss *Hyophila involùta* has showed various concentration of atmospheric PAHs around two studies areas but difficult to distinguished emission sources due to the urbanization and industrialization. Therefore, the pilot studies to be introduced around specific emission sources using moss *Hyophila involuta* as PAHs bioindicator to identify the relationships of ambient air PAHs and the emission sources.

CONCLUSION

Atmospheric deposition of PAHs in moss *Hyophila involuta* around Sapugaskanda oil refinery and Kelanitissa power plant is comparatively higher than Sinharaja rain forest area where the anthropogenic sources are minimum. The comparative results to be confirmed using instrumental air monitoring methods and developing of correlation between biomonitoring and actual air monitoring is needed as future studies.

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