A Comparison of Heavy Metal Deposition in two Metropolitan Areas in Western Province of Sri Lanka Using the Moss Biomonitoring Method

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Abstract
Air pollution by heavy metals has become one of the current environmental issues worldwide. Sri Lanka is also affecting this problem mainly due to the petroleum and petroleum-derived industries. Therefore, the magnitude of heavy metals in air and their emission sources are needed for making the policies to control air pollution. Biomonitoring is a cost-effective and environmentally friendly air monitoring technique and in the present study moss Hyophila involuta was used as a biomonitor to monitor the atmospheric deposition of heavy metals in the western province of Sri Lanka in the vicinity of the Sapugaskanda oil refinery and the Kelanitissa power plant. Moss samples and relevant soil samples were collected in March 2013 and in January 2014 and the concentrations of Fe, Zn, Cu, Pb, Ni, Cr and Cd by atomic absorption spectrometer (AAS) were determined.

The results obtained from the principal components analysis revealed that the elements can be grouped into two different components that indirectly reflected two different anthropogenic sources and Zn, Cu, Pb, Ni and Cr are believed to have originated from petrochemical-based applications operating around the studied area.

Keywords: Air pollution, Biomonitoring, Colombo, *Hyophila involuta.*

Introduction

Atmospheric pollution by heavy metals over large areas for a long period may cause chronic damage to living organisms and must be carefully controlled. Monitoring of atmospheric precipitation regularly has become an essential part of controlling the air pollution sources by providing suitable environmental planning and control programmes.

The use of mosses as pollution biomonitors is a convenient method to determine levels of atmospheric deposition because the terrestrial mosses were obtained most of their mineral elements directly from precipitation and dry deposition of airborne particles and have a great capacity to retain them on mosses[1,15]. The moss monitoring technique was first introduced in Scandinavia for studying atmospheric deposition of heavy metals[15].

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Thereafter moss biomonitoring has expanded in many regions in the world to determine heavy metal deposition in large scale studies close to industrial installations, lead-zinc smelters, power plants, aluminium production factories etc. and not expected to be contaminated with heavy metals in remote areas[2,6,17].

In comparison with other South Asian countries, Sri Lanka probably makes a greater effort to conserve its environment. Controlling air pollution is one of the challenges. Therefore, air monitoring should be implemented to make effective environmental policies and take urgent action to protect the nation's atmosphere for the sake of current and future generations. Even though the biomonitoring technique is widely known as an economical friendly air monitoring tool for assessing trace element atmospheric deposition, there were very few records of using this tool for investigating heavy metals in Sri Lanka.

However, background levels of heavy metals in six plant species have been analysed including a *Pogonatum* sp. (a moss) to represent the different taxonomic groups from a montane rain forest in Sri Lanka[10]. Moss *Hyophila* sp. has been used to monitor the atmospheric deposition of heavy metals in Kandy mainly due to the automobile traffic activities[19]. Even though Colombo is the commercial capital of Sri Lanka with a lot of industrial activities, road traffics (peak road traffic hours usually between 6.00 a.m to 8.30 a.m and 4.00 p.m to 7.30 p.m.) and developing projects (road and building construction), source identification study using moss have not been carried out yet.

Therefore, the current investigation was conducted to monitor the atmospheric deposition of heavy metals around two metropolitan areas in the western province in Sri Lanka using moss species *Hyophila involuta* as a biomonitor and to investigate the possibility of identification of heavy metal emission sources by the combined effect of heavy metals from known anthropogenic sources in Colombo; the Sapugaskanda oil refinery and the Kelanitissa power plant.

Material and Methods

Moss samples and corresponding soil samples were collected in sixteen sampling stations around the Sapugaskanda oil refinery and the Kelanitissa power plant. Sampling sites are located in the west coast of Sri Lanka within the range of latitude from 6° 56′ N to 6° 58′ N and the range of longitude from 79° 52′ E to 79° 58′ E with temperate climate influenced by the southwest monsoon (late May to

September) and the northeast monsoon (November to March) that results in heavy rainfall to the state. The area is generally fairly warm temperature and is humid throughout the year.

Ten sampling sites were selected area around the Sapugaskanda oil refinery which is approximately 18 km away from the commercial capital of Colombo in the direction of North East and known to be as the biggest 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' 42.48" N, 79° 57' 36.36" E), the 51 MW Asia power station (6° 57' 54" N, 79° 57' 28" E), the 22 MW Lak Danavi power station (6° 57' 29" N, 79° 57' 05" E) and several industries mainly the Lanka industrial estates (Lindel) located in Sapugaskanda on 125 acres of land and 19 industries are presently operating.

Six sampling sites were selected area around the Kelanitissa power station which is located within latitude 6° 57′ 8″ N longitude 79° 52′ 44″ E on the south bank of the Kelani river in the northern part of the city of Colombo and approximately about 6 km away from the commercial capital of Colombo. The transport network including port access road is considered to be the point source of the emission to the surrounding atmosphere.

Moss sampling technique and related procedures were based on the Scandinavian guidelines[9,14]. Moss *Hyophila involuta* and the relevant soil samples were collected in March 2013 and January 2014 and the sampling points were at least 300 m away from main roads, villages and 100 m from minor roads and buildings. At each sampling site, on an average 5 subsamples were taken within an area of 50×50 m^2 and a collective sample was taken into a plastic bag and carefully closed to prevent contamination during transportation and the samples were transported to the laboratory at 8 ºC using a cooled box. Plastic gloves were used when picking up the mosses thought out the sampling and analysis.

The green and green-brown parts of moss species corresponding to three years of growth were recommended for the analysis[9]. Therefore, the green or green-brown parts of the moss were used for further analysis. The samples were carefully cleaned from all dead material and attached litter and washed twice using deionized water to remove the unbounded metal particles from the moss surface. The samples were dried to a constant weight at 40 ºC. The representative samples of each moss species were prepared in triplicate.

Moss samples (500.0 mg of dry weight) were placed in a Teflon vessel and digested in concentrated HNO_3 (10.0 cm^3) for 15 min at 200 ºC using microwave accelerated reaction system (CEM Mars 6) with the following time program; ramp time for 20 min, hold time at 200 ºC for 15 min and cooling time for 20 min. The digested sample was filtered through a filter paper (MN 617 ≡ No. 4). The filtrate volume was transferred to a volumetric flask (25 cm^3) and made up to volume with deionized water. The samples were transferred to polypropylene bottles (50 cm^3) and kept in a refrigerator at 4 ºC until analysis.

The same procedure was followed for the digestion of blank, the reference material NIST SRM 1575a (pine needle) and the relevant soil sample. The metal contents Fe, Zn, Cu, Pb, Ni and Cr in the filtrate were determined by FAAS (GBC 932 plus) using an air-acetylene flame. Cd in the filtrate was determined by GFAAS (Analytikjena novAA 400P) using N_2 as an inert gas. To determine the accuracy of the analysis, NIST SRM 1575a (pine needle) was treated in the same manner as the moss samples.

The enrichment factors (EFs) were determined to identify the presence of anthropogenic contaminants using Fe as the reference element[5]:

$$EF = \frac{(X_{moss}/Fe_{moss})}{(X_{soil}/Fe_{soil})}$$

where X_{moss} and Fe_{moss} are concentrations of element X and Fe in moss sample and X_{soil} and Fe_{soil} are concentrations of element X and Fe in the relevant soil sample.

Table 1
Analysed of NIST 1575a pine needles reference material

Element	Certified value (mg kg^{-1})	Observed value (mg kg^{-1})	Recovery (%)
Fe	46 (±2)	48 (±2)	104
Zn	38 (±2)	39 (±1)	103
Cu	2.8 (±0.2)	2.7 (±0.1)	97
Pb	0.167 (±0.015)	0.160 (±0.008)	96
Ni	1.47 (±0.1)	1.49 (±0.02)	101
Cr	0.3–0.5	0.4	75–125
Cd	0.233 (±0.004)	0.229 (±0.007)	98

Statistical comparison of means of EF values was performed using one-way ANOVA ($p < 0.05$) for the normally distributed set of data and the heavy metal concentration data was also subjected to principal component analysis (PCA) and component analysis (CA) using a statistical package (SPSS 16).

Results and Discussion

The accuracy of the microwave digestion procedure was tested using standard reference material (NIST 1575a pine needles) and the results are given in table 1. The concentrations of heavy metals in moss and the relent soil were calculated by dry weight basis (mg kg^{-1}) and the basic statistic parameters for all metals (Zn, Cu, Pb, Ni, Cr and Cd) determined in moss *Hyophila involuta* for two sampling locations Sapugaskanda oil refinery (S) and Kelanitissa power plant (K) are given in table 2.

The concentrations of seven elements (Fe, Zn, Cu, Pb, Ni, Cr and Cd) in relevant soil samples were also analysed to determine the EFs of six elements to Fe for each sampling site. The concentrations of conservative soil elements Al, Si, or Ti have been also used for the calculation of EFs instead of Fe[8]. The average EFs with statistical analysis (one-way ANOVA, $p < 0.05$) are summarized in table 3.

Table 2
Summary statistics of heavy metal concentrations (mg kg^{-1}) in the analyzed moss samples collected around Sapugaskanda oil refinery(S) and Kelanitissa power plant (K) in March 2013 and in January 2014

Location: Month	Concentration of heavy metal in moss (mg kg^{-1})					
	Zn	Cu	Pb	Ni	Cr	Cd
S: March 2013						
Average	302.90	25.51	24.06	42.52	36.41	0.52
SD	207.60	6.39	13.28	17.46	18.91	0.15
Minimum	109.20	18.35	6.31	25.97	20.35	0.35
Maximum	811.30	39.40	46.28	69.60	80.20	0.85
S: January 2014						
Average	247.80	18.99	38.60	35.29	22.59	0.50
SD	124.80	6.98	31.90	24.20	8.51	0.24
Minimum	67.30	10.23	20.10	18.03	12.65	0.11
Maximum	490.50	31.88	127.00	91.14	38.35	0.88
K: March 2013						
Average	645.50	38.07	38.70	38.50	29.40	0.53
SD	442.00	24.40	33.80	12.09	10.71	0.15
Minimum	199.90	12.10	6.80	26.10	17.89	0.35
Maximum	1087.00	70.20	93.60	57.68	49.71	0.70
K: January 2014						
Average	384.50	48.70	40.32	20.29	12.25	0.53
SD	102.00	27.40	22.31	4.13	2.87	0.19
Minimum	287.80	31.70	13.41	14.88	8.15	0.27
Maximum	533.10	97.20	74.24	26.00	16.25	0.78

Table 3
Means EFs of six elements in moss relative to the soil, the area around the Sapugaskanda oil refinery and the Kelanitissa power plant

Heavy Metal	Sapugaskanda oil refinery			Kelanitissa power plant	
	March 2013	January 2014		March 2013	January 2014
Zn	11.4(±2.5)^{a*}	13.9(±3.1)^{a}		17.6(±5.8)^{b}	19.4 (±5.9)^{b}
Cu	8.0(±3.2)^{a}	9.5(±2.8)^{a}		11.2(±5.8)^{a}	11.6(±5.1)^{a}
Pb	12.0(±5.7)^{a}	12.1(±3.8)^{a}		11.6(±5.7)^{a}	12.6(±4.2)^{a}
Ni	8.4(±5.0)^{a}	11.0(±5.2)^{a}		16.2(±3.5)^{b}	12.3(±2.3)^{a}
Cr	7.7(±4.2)^{a}	9.9(±2.8)^{a}		14.3(±6.3)^{b}	12.2(±2.9)^{ab}
Cd	3.2(±1.3)^{a}	4.5(±1.6)^{a}		6.3(±2.7)^{a}	5.8(±1.9)^{a}

*Different letters indicate significant differences between means (ANOVA, $p < 0.05$) of the same element

The EFs obtained from the Sapugaskanda oil refinery showed no significant difference between the EFs for each element observed in this study for two months while the EFs obtained for the Kelanitissa power plant area showed no significant difference between the EFs for five elements except Ni.

The comparison of EFs in the two sampling locations showed a statically significant difference between them for the element Zn. Even though concentrations of some heavy metals in moss fluctuated during the two months, the variation of EFs was not significant.

The EFs can be used to classify the sources of heavy metal fallout. The normal assumption is that most of the Fe found in moss tissue is of terrestrial origin; thus, EF ≥ 10 indicates that the concentration observed in moss could be of anthropogenic origin and EF < 10 indicates that the concentration observed in moss is likely to be predominantly of natural sources, either soil or substrate. The EFs are calculated from the concentration of heavy metals in the soil and mosses but moss accumulates only bioaccessible forms of heavy metals. Even though some authors argued that EF < 10 is merely the measurement background, the use of EF < 10 to assess the origin of emission sources showed uncertainty with the analytical method and inhomogeneity of the chemical composition of samples[12].

The high EFs (≥ 10) were observed for the elements Zn, Cu, Pb, Ni and Cr except for Cd. Among the elements, the EFs of Zn and Pb were higher than 10 and showed that Ni, Cr and Cu were close to 10 around the Sapugaskanda oil refinery whereas the higher EFs were seen for Zn, Cu, Pb, Ni and Cr for the area around the Kelanitissa power plant. Therefore Zn, Cu, Pb, Ni and Cr seem to be originated from point anthropogenic sources around the area.

The heavy metal concentration data were also subjected to principal component analysis (PCA) and the plot of scores (the sites), the loadings (weight of metal concentrations on the linear combination PCs) and the plot of score summarized the information about the similarities between the sites and between the metal concentrations. PCs were chosen according to Kaiser's criteria which accepted only PCs with Eigenvalues more than one[11]. Total variance explained by the first two principal components (PC) and component matrices is given in table 4.

According to table 4, the total variance explained by the first two components was 60.3%. The factor loadings for heavy metals analyzed are given in table 5.

The first component PC1 included the metals of Pb, Cu and Zn while the second component PC2 contained the elements of Ni, Cd and Cr. Further cluster analysis of metal concentrations revealed the same correlation between the elements. The results obtained for cluster analysis are presented as a dendrogram (Figure 1), where the distance cluster represents the degree of association between the elements. The lower is the values of the distance cluster, the more significant is the association.

Table 4
Principal component analysis (PCA) statistics on the matrix of elemental concentrations in moss for the studied area

	Initial eigenvalues			**Extraction sums of squared loadings**			**Rotation sums of squared loadings**	
	Total	**Var %**	**Cum %**	**Total**	**Var %**		**Total**	**Var %**
1	2.233	37.225	37.225	2.233	37.225		2.228	37.129
2	1.387	23.119	60.344	1.387	23.119		1.393	23.215
3	0.885	14.744	75.088					
4	0.809	13.476	88.564					
5	0.566	9.439	98.003					
6	0.120	1.997	100.000					

Extraction method: principal component analysis; rotation method: varimax with Kaiser normalization.

Table 5
Factor loadings for the analyzed moss samples for the studied area (after varimax rotation)

Heavy metal	**PC1**	**PC2**
Pb	0.956	0.009
Cu	0.855	-0.143
Zn	0.700	0.303
Ni	-0.123	0.755
Cd	0.198	0.595
Cr	-0.209	0.593

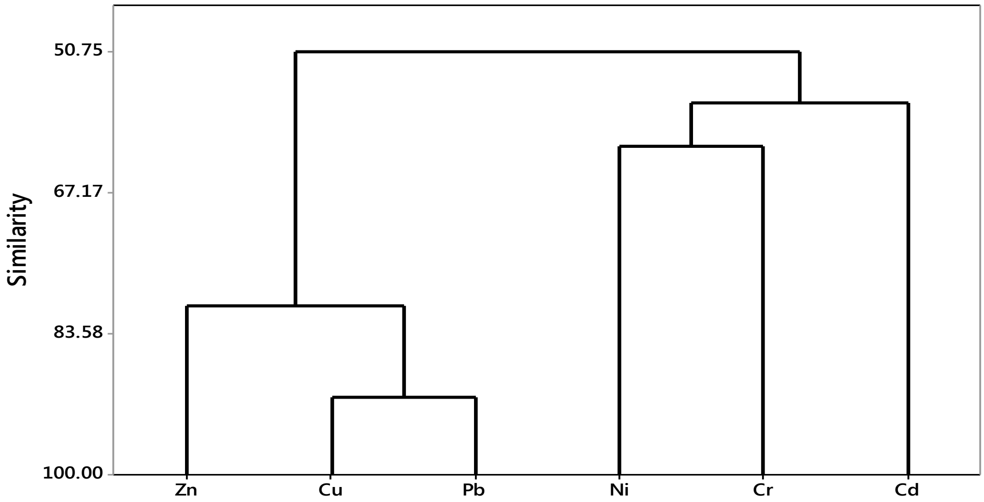

Figure 1: Dendrogram obtained by hierarchical cluster analysis of heavy metal content in moss around Colombo (the distances reflect the degree of correlation between elements)

Combustion of leaded, low-leaded and unleaded gasoline continues to be the major source of atmospheric Pb emissions and non-ferrous metal production, which is the largest source of atmospheric Cu and Zn[13]. Road transportation is also the largest contributor for Zn, Cu and Pb emissions. Vegetation factor and soil factor also play important roles in the elevation of the metals Zn and Cu in ambient air[18]. By EF results (EF > 10), anthropogenic activities were the dominant factors in localities with a high accumulation of Zn and Pb. According to PCA, Cu appeared in the PC1 factor with the group of elements Zn and Pb. However, the EF of Cu was close to 10. In the literature, it has been stated that Zn, Cu and Pb mainly arise from anthropogenic sources[7].

Therefore, high concentrations of these three elements in two selected sampling locations showed that these elements originate from anthropogenic sources. The area around the Kelanitissa power plant shows higher traffic congestion than the Sapugaskanda oil refinery area and traffic congestion increases the tire waste which has been identified as a major anthropogenic source of Zn[4]. Therefore, PC1 was compatible with the Kelanitissa power plant area as well as with the pollutants from road transportation.

Considerable amounts of Cr, Ni and Cd are linked to the emissions from a power station and to other industries where petroleum-derived products are burned. The presence of Cr is mainly associated with soil lithology. Steel and iron production works are mostly concentrated with Cr and Ni in these two locations. EFs for Cr and Ni were closer to 10 in the area around the Sapugaskanda oil refinery and greater than 10 for the area around the Kelanitissa power plant. EF for Cd (EF < 10) represents the origin of pollution as natural sources (either soil dust or substrate).

For each moss sample, a score can be derived that represents the importance of each factor in determining its composition (Table 4). It has been classified that factor loading 0.3 is generally considered the cutoff point; over 0.4 to 0.7 is classified low to moderate and above 0.8 is strong or good[3]. In this study, Zn can be included in both PC1 and PC2 factors and more correlated with PC1 than PC2. This indicates that the measured concentration of Zn is predominantly derived from two different anthropogenic sources.

Since PC1 seems to represent road transportation pollution sources near the area around the Kelanitissa power plant, PC2 seems to represent the power stations and petroleum-related industries around the selected areas. Therefore, the relationships among the elements can be used to identify the point emission sources around the studied areas.

Metal concentrations in moss tissues have been statistically correlated with environmental and climatic factors as well as with bulk deposition of elements and elemental concentration in soil[7]. However, the sampling months January and March lie to NE monsoon season and first inter-monsoon season in Sri Lanka respectively and the effects of climatic factors for the west part of Country are minimum during this period.

Conclusion

The combination of enrichment factor analysis and multivariate analysis has revealed much about the origin of the fallout of heavy metal pollution and except Cd, all other studied heavy metals (Zn, Cu, Pb, Ni and Cr) originated predominantly from anthropogenic emissions. The possible sources can mostly be explained by petroleum and petrochemical activities such as oil refinery, power plants and road transportation. Besides industrial activities, construction works, population densit and some local sources may have affected the heavy metal accumulations in the study region.

The highest concentrations of Zn, Pb and Cu were seen near to Kelanitissa power plant location where the location showed considerably higher road transportations than the area around Sapugaskanda oil refinery and Ni and Cr are believed to have originated from local petrochemical-based industries operating around Colombo sampling location i.e. Sapugaskanda oil refinery, power plants.

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