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DETERMINATION AND SOURCE APPORTIONMENT OF SELECTED HEAVY METALS IN AEROSOL SAMPLES COLLECTED FROM SEBELE

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ABSTRACT

Bush fires and dust in the dry winter months establish moderately high background levels of aerosols. Emissions into the atmosphere by copper mines, coal mines and vehicular emissions are all possible sources of air pollution with heavy metals. Although there has been assessment and monitoring of heavy metals and their air pollution in other countries such as Brazil, Europe and America, there is little documentation about concentration of heavy metals in aerosols in Botswana. A total of 63 Aerosol samples were collected at the Botswana College of Agriculture and were analysed for concentrations of Al, Co, Cu, Fe, Pb, Mn, Ni and Zn in filtrate using a Flame Atomic Absorption Spectrometer (Varian SpectrAA 220 FS). Statistical receptor models were applied to investigate potential sources of the studied metals. Data exhibits enhanced enrichments of Zn (EF_g = 76), Al (EF_g = 14391), Co (EF_g = 19), Cu (EF_g = 5), Pb (EF_g = 3) and Ni (EF_g = 2), which was attributed to contributions from non-crustal sources, whereas Mn and Fe (EF_g < 2) were attributed to crustal origin, such as airborne dust. Data was subjected to factor analysis (FA) twice. From FA-1, two Principal Components (PC) were revealed. PC-1 showed high positive loadings of Pb, Zn, Ni and Al, whereas PC-2 had loadings for Fe and Mn. On the other hand, FA-2 had three principal components. PC-1 from FA-2 showed strong loadings for Cu, Fe and Mn. FA-2 had strong loadings of Pb, Al and Zn, whereas loadings for PC-3 were comprised of Ni and Co. The difference between loadings of FA-1 and FA-2 suggested possibilities of mixed origins of the studied metals. Finally, air mass back-trajectory analysis showed that during the sampling period, there were only 5 cluster groups that represented significantly different transport pathways of aerosol samples, where only Zn and Ni mean concentrations revealed dependence on geographical origin of aerosol samples. Results of the analysed concentrations of Al, Co, Cu, Fe, Pb, Mn, Ni and Zn in aerosol samples showed that the presence of Fe and Mn in the atmosphere in the ambient air of Sebele is mainly due to contributions from lithogenic sources. Pb, Ni, Co, Al and Zn exist because of anthropogenic sources, whereas, Cu, exist because of mixed origins. Trajectory analysis further shows that the anthropogenic Zn and Ni could also be present in the air sampled due to air mass transportation from distant sources.

Keywords: Heavy Metals, Geometric Enrichment Factors, Factor Analysis, Back-Trajectory Analysis, Studied Metals, Different Transport, Anthropogenic Sources, Principal Components (PC)

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1. INTRODUCTION

Research has recognised certain metals such as iron (Fe), Zinc (Zn), Chromium (Cr), Selenium (Se), Copper (Cu) Iodine (I) Cobalt (Co) and Molybdenum (Mo) as essential, in trace amounts, in human health and plant nutrition. However, findings have shown exposure to elevated levels of certain metals to exhibit health problems (Ghio and Devlin, 2001; Schaumann *et al*., 2004; Wang *et al*., 2008). Therefore, reduction of air pollution to some acceptable levels is an important environmental issue (Dimov *et al*., 2004).

The main input for many of these elements is related to particle emission sources (natural and anthropogenic). Anthropogenic sources include fossil fuel combustion, vehicular emission, industrial activities, energy production, construction and waste incineration; whereas wind eroded soil dust and forest fires may contribute to natural bearing sources. Previous similar studies report that increased concentrations of As, Cd, Cu, Ni and Zn are due to metallurgic processes (Bilos *et al*., 2001; Wang *et al*., 2005). Fe and Mn can be emitted from industrial processes and from Earth's crust (Mugica *et al*., 2002; Lopez *et al*., 2005; Wang *et al*., 2005). Ni and Zn can also be produced by vehicular emission and oil fuel consumption (Allen *et al*., 2001; Espinosa *et al*., 2001; Wang *et al*., 2005).

Atmospheric metal concentrations exhibit both spatial and temporal variations since they are dependent of the distances to the sources and meteorological variables, respectively (Gharaibeth *et al*., 2010). Studies have also shown short-term differences of atmospheric metal concentration on a day-to-day or even hour-to-hour-basis (Silvia *et al*., 2004; Velde *et al*., 1998; Var *et al*., 2000; Munir and Shaheen, 2008).

A number of heavy metals in aerosol samples were determined in different countries such as Brazil (Silvia *et al*., 2004), USA (Yang *et al*., 2002) Portugal (Vasconselos and Tavares, 1998), Russia (Drobyshev and Emelina, 2001) and international and national continuous monitoring programs for regulatory purposes such as the European Monitoring and Evaluation Program (EMEP). However, literature is scarce for most African developing countries such as Botswana.

Botswana is a lightly industrialized country with a relatively sparse population and pollution is probably not perceived to be a major problem at present. However, widespread vegetation fires and dust in the dry winter months establish moderately high background levels of aerosols and ozone. The copper smelter, located in the eastern part of the country at Selibe-Phikwe is a significant source of metallurgical fine dust emissions, enriched with toxic elements, that is, Ni, Cu, Pb, Zn and As, followed by the emissions of ultra-fine fly ash particles enriched with Co, Pb and Mn from the coal powered Morupule Power Station in Palapye, which are approximately 400 and 300 km north east of the sampling station, respectively. Vehicle use within Gaborone and other major towns such as Francistown, Maun and Serowe could be a future source of air pollutants. Increased growth of light industry could also lead to greater air pollution impacts in the future.

Generally, the climate controls of Botswana are influenced by the prevalent subtropical high-pressure belt that is dominant over southern Africa, which is, except in a few winter months (May-July), split by the continent to become the Atlantic Ocean High and the Indian Ocean High. The country has a semi-arid climate, with highly variable rainfall, both spatially and temporally. On annual averages, rainfall ranges from 250 mm in the extreme southwest and 650 mm in the extreme north (Batisani and Yarnal, 2010). The seasons are characterized by November-January (summer), February-April (autumn), May-July (winter) and August-October (spring). The summer months are generally wet and hot (18-40°C), while the winter months are dry and cold (-5-18°C).

The aim of the study was to: (1) investigate levels of heavy metals: Al, Co, Cu, Fe, Pb, Mn, Ni and Zn in air collected from a sampling site in Sebele, (approximately 8 km from the capital city, Gaborone) Botswana, (2) evaluate the content of heavy metals in ambient air with respect to meteorological variables such as wind speed and precipitation, (3) identify the main heavy metal sources in particulate matter by applying receptor-modelling techniques and finally (4) locate geographically potential source regions that can contribute to heavy metal levels via transport processes using statistical analysis of back-trajectories.

2. MATERIALS AND METHODS

The study area: The sampling site was located at the Botswana College of Agriculture, Sebele (24.59°S, 025.94°E; 1004 m ASL); approximately 8 km from the capital city of Botswana, Gaborone (**Fig. 1**).

2.1. Sampling Strategies and Analysis

Aerosol samples were collected with a high volume sampler placed on the roof top of a 10 m tall building at the Botswana College of Agriculture. The flow rate was set to 1.7 m^3 min^{-1}. Three-day (72-h) continuous sampling was performed to pass an air volume of approximately 5000 m^3 through 20.3 cm×24.5 cm Glass Fibre Filter papers. The filters were weighed before and after the sampling using a microbalance to obtain the net mass of collected particles.

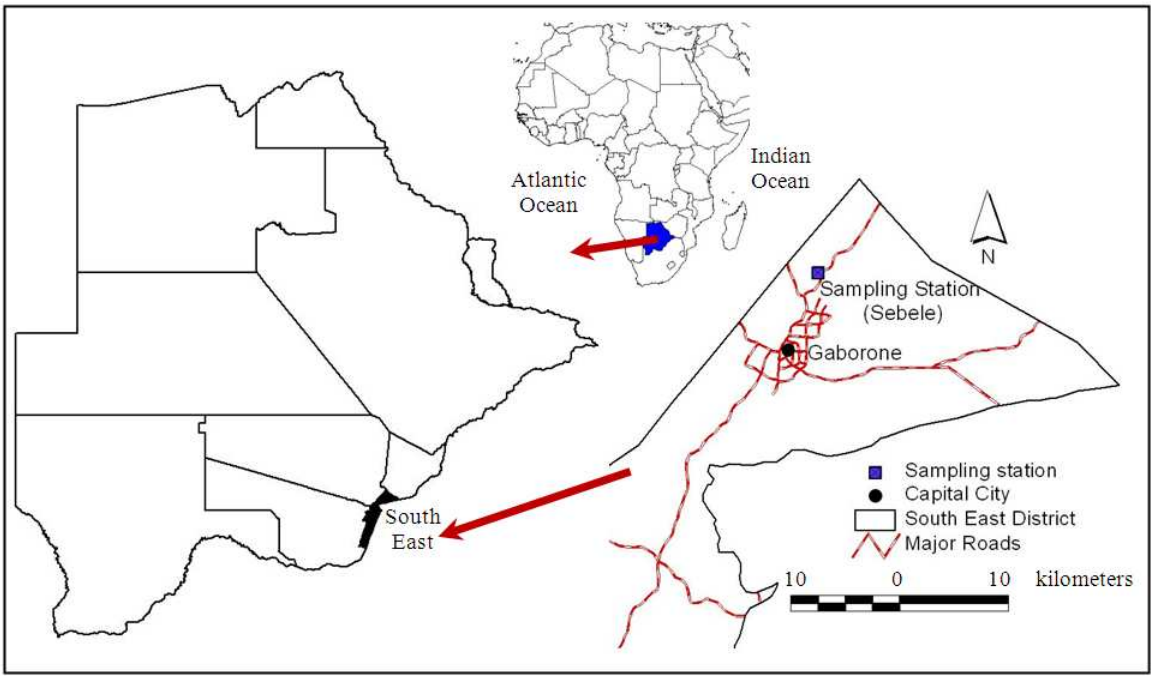


Fig. 1. Map of Botswana showing the sampling site in this study

From each filter paper, samples of 0.50 g were digested in 20 mL freshly prepared aqua regia (1:3 HNO_3: HCl) on a hot plate for 3 h. After evaporation to dryness, samples were re-dissolved in 20 mL of 1% HNO_3, filtered through a 0.45 µm filter paper and then transferred into a 100 mL volumetric flask. The flask was filled to the mark with 1% HNO_3 v/v (diluted in deionised H_2O). Standard reference material was prepared using stock solution from SAARCHM and MERCH and was used to have a check on the accuracy of the results. The total concentrations of Al, Co, Cu, Fe, Pb, Mn, Ni and Zn in filtrate were then determined using a Flame Atomic Absorption Spectrometer (Varian SpectrAA 220 FS) at wavelengths, λ: Al = 309.3 nm; Co = 240.7 nm; Cu = 324.8 nm; Fe = 372.0 nm; Pb = 217.0 nm; Mn = 279.5; Ni = 232.0 nm and Zn = 213.9 nm, using air acetylene flame.

2.2. Data treatment

Enrichment Factors (EF) of heavy metals in aerosol samples were determined based on the crustal abundances of elements given by Taylor (1964). Usually, Si, Al or Fe is used as the reference element, but there is no universally accepted rule for its choice. In this research, Fe was used as a reference element because natural sources (~98%) vastly dominate its input (Tippie, 1984), as done previously by other investigators (Bilos *et al*., 2001; Manoli *et al*., 2002). The geometric mean enrichment factor EF_g calculation methodology for individual heavy metal was determined by Equation 1 (Kulshrestha *et al*., 1995):

$$EF_g = \exp\left[\frac{1}{N}\sum_{i=1}^{N}\ln EF_i\right] \quad (1)$$

where, N is the number of data points and EF_i is the enrichment factor of the ith point determined by Equation 2:

$$EF = \frac{(Element/Fe)_{Air}}{(Element/Fe)_{Crust}} \quad (2)$$

where, $(Element/Fe)_{Air}$ and $(Element/Fe)_{Crust}$ refer to concentration ratios of element to Fe in air and crust, respectively. Elements which have EF_gs up to 2 are not considered to be enriched. Elements with $2<EF_g\leq20$ are moderately enriched and elements with $EF_g>20$ are considered to be highly enriched and have different sources than the crust.

2.3. Statistical Analysis

Correlation of different elements in air samples and meteorological parameters were calculated by the non-

parametric Spearman Rank method. To help the identification of different metal types, Principal Component Analysis was performed to establish possible factors that contribute towards the metal concentrations and source apportionment. All data set was subjected to Factor Analysis (FA). The number of significant Principal Components (PC) was selected on the basis of Varimax orthogonal rotation with Kaiser Normalisation with eigenvalues greater than 1.

2.4. Back-Trajectory Analysis

Three-day back trajectories arriving at Sebele (24.59°S, 025.94°E) were computed using the PC Version 4.9 of the National Oceanic and Atmospheric Administration (NOAA)'s Air Resources Laboratory (ARL) Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) (Draxler and Hess, 2004) for the sampling period (April-December 2008). The model was run using Global Data Assimilation System (GDAS) archived meteorological data to determine air mass origins. As a control measure for self consistency, trajectories were run three times daily with ending times of 06h00, 12h00 and 18h00 UTC (Coordinated Universal Time). Three different pressure levels corresponding to 500, 1000 and 1500 m Above Ground Level (AGL), were run to determine the possibilities of shear within each six-h time step. Trajectories found to have substantially different paths within the 500, 1000 and 1500 m AGL for a given model run were excluded from the calculations to avoid the possibility of shear in airflow. Then, only the 72-h back trajectories arriving at 12h00, 500 m AGL were considered in the calculations. The choice for 72-h back trajectories is supported by the fact that the mean aerosol lifetime is ~3 days whereas the 500 m elevation was considered to be within the mixing layer of the atmosphere. The arriving time of 12h00 UTC was chosen arbitrarily since there were no observed differences in trajectory paths between the 06h00, 12h00 and 18h00 ending times.

The measured metal concentration data for each element analysed were then associated with their corresponding 72-h back trajectory arriving at the sampling site to identify potential source regions. This was achieved by computing t-tests to determine whether the average metal concentrations associated with each cluster were significantly different.

3. RESULTS

The time series data of aerosol samples together with precipitation and wind speed during sampling period are displayed in the Appendix. Data revealed enhanced mean concentrations of Al ($t = 10.57$; $df = 61$; $P = 0.0000$) and Zn ($t = 26.61$; $df = 61$; $P = 0.0000$) for aerosols measurement collected during 02/04/08-19/05/08 are as follows; (3900±1400) ng/m^3 for Al and (1400±560) ng/m^3 for Zn, compared to those obtained during the rest of sampling periods; (2300±680) ng/m^3 for Al and (60±20) ng/m^3 for Zn. Similarly, Pb was observed to exhibit a higher mean concentration (6±2) ng/m^3 during the same period but almost undetectable in most samples during the rest of the period. Nickel exhibits a high mean concentration ($t = 4.67$; $df = 14$; $P = 0.0004$) of (4 ± 1) ng/m^3; during the 02/04/08–19/05/08 period as compared to the period 13/11/08-07/12/08 (5±1) ng/m^3; mean concentration = (1.3±0.3) ng/m^3 but somewhat variable (0.01-1.76) ng/m^3 to no detection in between. Cobalt, however, showed relatively lower mean concentrations of (1.2±0.3) ng/m^3 ($t = 8.92$; $df = 14$; $P = 0.0000$), during the 02/04/08-19/05/08 period as compared to the period 13/11/08-07/12/08 (5±1) ng/m^3. There was no observable pattern in mean concentrations throughout the sampling period for the other studied (Cu, Fe and Mn) metals.

The aerosol data were log-normally distributed. The geometric mean and geometric standard deviations of the heavy metals with guidelines for specific metals are given in **Table 1**. Observations showed a high variability (min-max) in the metal concentrations of each metal.

Figure 2 present results of geometrical enrichment factors of the metals. The EF_gs values of Zn ($EF_g = 76$) and Al ($EF_g = 14391$) showed high enrichment of metals. Co ($EF_g = 19$), Cu ($EF_g = 5$) Pb ($EF_g = 3$) and Ni ($EF_g = 2$) are moderately enriched. Thus, these metals can be considered to possess contributions from non-crustal sources, whereas Mn and Fe ($EF_g<2$) could be of crustal origin, such as the airborne dust.

Table 2 shows correlation between metals and some meteorological parameters (rainfall and wind speed). Significantly high negative correlation ($P = 0.001$) were observed between Cu, Fe, Mn, Ni and Pb with wind speed. Rainfall also revealed high ($P = 0.001$) negative correlations with Cu, Fe and Mn. No significant correlations were however observed between rainfall and Al, Co, Ni, Pb and Zn. Similarly, there were no significant correlations between wind speed and Al, Co and Zn. Inter-elemental correlations were also observed between some metals.

Due to the observed mean concentrations differences of Al, Zn, Pb and Ni metal contents in aerosols for the dates 02/04/08-19/05/08 compared to means for the rest of sampling periods, data sets were subjected to factor analysis twice: (1) with all data set combined together (FA-1) and (2) data for 25/05/08-07/12/08 (FA-2).

Table 1. Basic statistics for the measured aerosol concentrations with guidelines for specific metals

	Measured metal concentrations (ng/m^3)			Emission guideline metal concentrations (ng/m^3)	
Metal	Min-Max	GM	GSD	Annual averages	Reference source
Al	493.82-5354.18	1452.04	1.32	–	–
Co	0.13-262.69	2.03	1.36	5	United Kingdom Air Quality Standards (UK, 2007)
Cu	0.94-35.43	2.74	1.24	–	–
Fe	37.22-1163.88	410.21	1.49	–	–
Mn	4.69-28.20	13.22	1.18	150	World Health Organizations (WHO, 2000)
Ni	0.01-5.96	0.67	1.79	20	United Kingdom Air Quality Standards (UK, 2007)
Pb	0.07-9.00	0.64	2.23	500	World Health Organizations (WHO, 2000)
Zn	13.30-3224.44	92.70	5.17	–	–

Table 2. The Spearman rho correlation coefficients between heavy metals rainfall and wind speed

	Al	Co	Cu	Fe	Mn	Ni	Pb	Zn	Rain	Wind
Al	1	0.34**	-0.05	-0.16	-0.07	0.31*	0.36**	0.66**	0.00	0.06
Co		1.00	-0.17	-0.39**	-0.37**	0.45**	0.50**	0.41**	0.17	0.15
Cu			1.00	0.56**	0.70**	0.13	0.22	-0.14	-0.42**	-0.40**
Fe				1.00	0.86**	0.05	-0.09	-0.27*	-0.48**	-0.34**
Mn					1.00	0.16	0.02	-0.20	-0.57**	-0.40**
Ni						1.00	0.59**	0.59**	-0.17	-0.43**
Pb							1.00	0.54**	-0.13	-0.43**
Zn								1.00	-0.01	-0.24
Rain									1.00	0.37**
Wind										1.00

**: Correlation is significant at the 0.01 level (2-tailed); *: Correlation is significant at the 0.05 level (2-tailed)

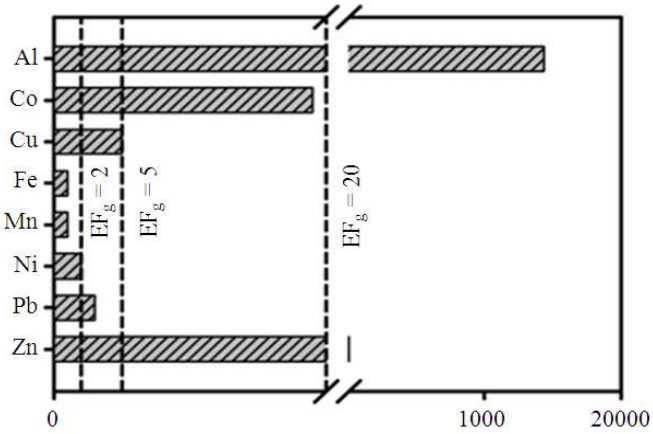


Fig. 2. Geometrical enrichment factors of the studied metals

3.1. Factor Analysis (FA-1)

Two principal components comprising 72.01% cumulative total variance were retained after Varimax othorgonal rotation, because subsequent eigenvalues were less than 1. The factor loadings are presented in **Table 3**. The first Principal Component (PC-1) accounting for 44.8% variance show high positive loadings of Pb, Zn, Ni and Al, whereas the second component PC-2 accounted for 27.8% of high positive loadings for Fe and Mn.

Cobalt and copper had very weak communalities (~0.4). This suggests that the two are not in common with other metals studied, as depicted in **Fig. 3**.

3.2. Factor Analysis (FA-2)

Factors Analysis (FA-2) revealed three component factors which comprised of 90.81% cumulative total variance (**Table 4**). PC-1 explains 43.41% of variance in the data set and has very strong loadings for Cu, Fe and Mn. The second principal component accounts for 25.57% of the variance and also has strong loadings for Pb, Al and Zn. The last Principal Component (PC-3) accounted for 21.83% of the variance in the data set, with strong loadings for Ni and Co.

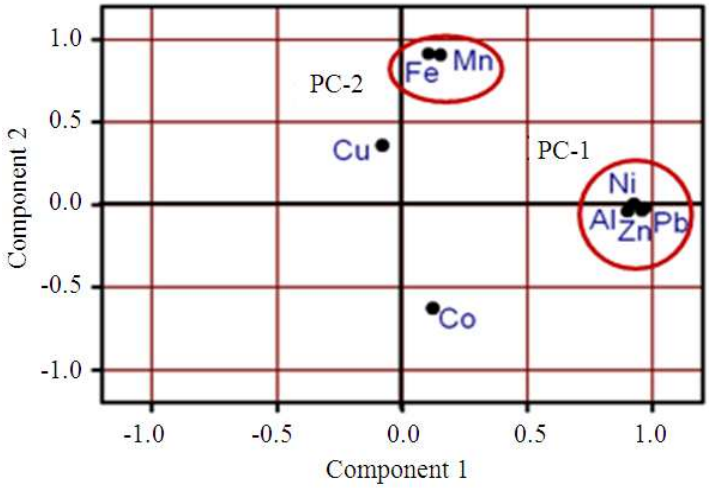


Fig. 3. Principal component analysis for the studied metals in FA-1

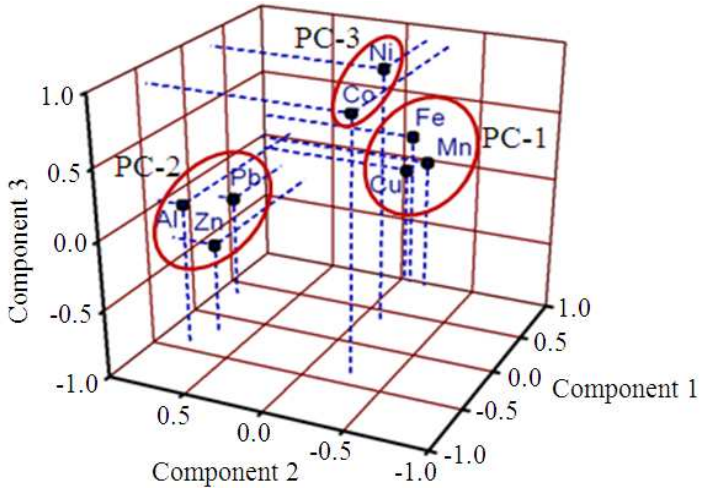


Fig. 4. Principal component analysis for the studied metals in FA-2

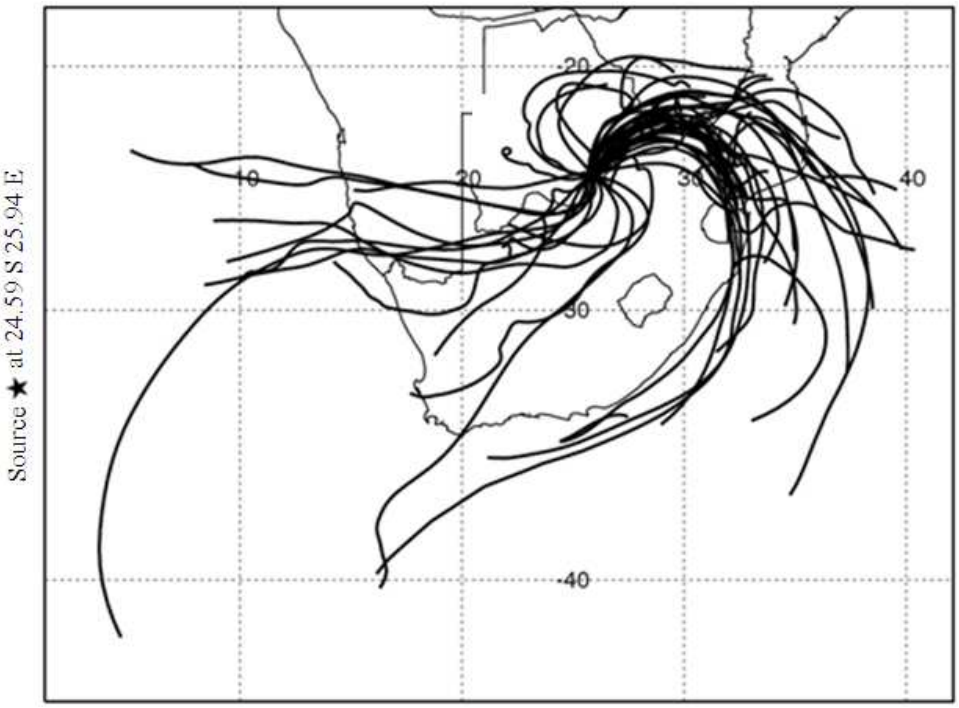
Table 3. Factor loadings and communalities of metals (FA-1)

Element	PC-1	PC-2	Communalities
Pb	0.968	-0.023	0.937
Zn	0.959	-0.036	0.920
Ni	0.926	0.004	0.858
Al	0.901	-0.043	0.813
Fe	0.106	0.912	0.842
Mn	0.154	0.907	0.847
Co	0.124	-0.629	0.411
Cu	-0.078	0.356	0.133
Eigen values	3.581	2.180	
% of Variance	44.761	27.251	
Cumulative %	44.761	72.013	

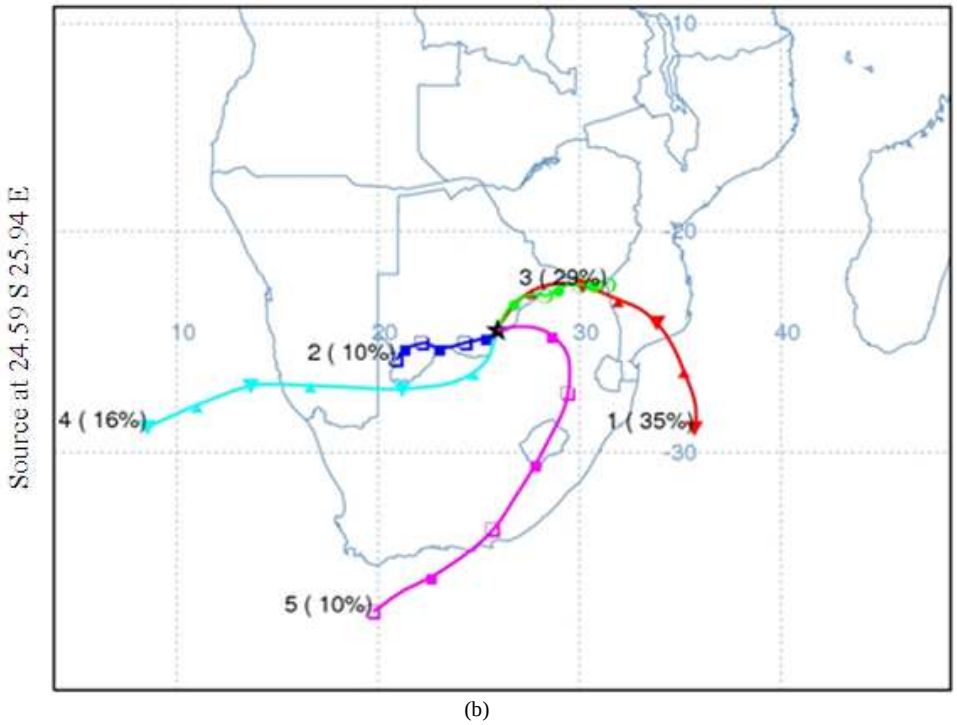
It is evident from the rotated component matrix depicted in **Fig. 4** that all the eight metals analysed were explained by three principal components. Furthermore, the communalities of the elements were very strong (>0.8), which indicates that retention of the three components was sufficient to explain all variances of the metals (**Table 4**).

3.3. Analysis of Aerosol Data with Trajectory Clustering

The air mass backward trajectories ending at the sampling station at an altitude of 500 m AGL for 25/05/08-07/12/08 sampling period using the HYSPLIT model are given in **Fig. 5**.



(a)



(b)

Fig. 5. (a) 72-hour backward trajectories and (b) the corresponding cluster means

Table 4. Factor loadings and communalities of metals (FA-2)

Element	PC-1	PC-2	PC-3	Communalities
Cu	0.987	-0.030	-0.097	0.984
Fe	0.983	-0.069	0.169	0.999
Mn	0.964	-0.178	-0.004	0.962
Pb	0.341	0.877	-0.234	0.940
Al	-0.395	0.805	0.043	0.806
Zn	-0.216	0.705	-0.316	0.643
Ni	0.345	-0.134	0.894	0.936
Co	-0.407	-0.275	0.868	0.994
Eigen values	3.473	2.045	1.747	
% of Variance	43.409	25.565	21.831	
Cumulative %	43.409	68.974	90.806	

Table 5. Trajectory membership, geometric mean and geometric standard deviation per cluster (CL 1–5)

	Geometric Mean ±Geometric Standard Deviation concentration per cluster (ng/m^3)					
Group 5 clusters	Al	Cu	Fe	Mn	Ni	Zn
CL 1	1280±460	2.6±1.0	410±230	12.4±5.6	0.9±0.5*	67±21
CL 2	1210±320	3.3±1.0	510±200	14.9±4.1	1.1±0.4*	80±22*
CL 3	1380±460	2.6±0.8	530±300	15.2±6.6	1.0±0.5*	63±20
CL 4	1560±730	6.7±11.6	470±240	12.7±6.7	0.3±0.4*	53±18*
CL 5	1000±280	3.1±0.7	500±140	13.4±3.7	0.6±0.8	51±28*
Total mean	1310±490	3.4±4.6	470±240	14.1±5. 5	0.8±0.5*	63±22*

*Metal concentrations are significantly different ($P < 0.05$) between clusters as will be explained in text.

From the 63 back trajectories generated, 51 were consistent in air flow and are thus shown in **Fig. 5a**. After applying cluster analysis, the cluster plot indicating the percentage change in total spatial variance as clusters were combined and suggested 4 cluster groups and their percentage changes as follows; 9 (57.19%), 5 (94.04%), 3 (46.32%) and 2 (252.45%). Cluster group 5 (94.04%) was then selected on the basis that it has enough clusters that represent different transport patterns and yet not so many to obscure the pattern (**Fig. 5b**).

The geometrical mean concentrations of heavy metals in aerosols for each cluster were then calculated. **Table 5** shows mean concentrations of heavy metals for data set sampled on 25/05/08-07/12/08. Mean concentrations for Co and Pb are not included since they were not detected in most of the samples during this study period (see Appendix).

In each group of elements; Al, Cu, Fe and Mn, geometric mean concentrations in air were not significantly different (at $p<0.05$) between clusters. A few cases were however observed between clusters for Zn (CL 2 versus 4, 5 and the total mean). Ni however exhibits a number of significant differences in mean concentrations (CL1 versus 4; CL-2 versus 4; CL-3 versus 4 and CL-4 versus the total mean).

4. DISCUSSION

Comparatively high mean concentrations of Al, Zn, Pb and Ni observed during sampling dates of 02/04/08–19/05/08 (bolded dates in Appendix) compared to concentration means for the rest of sampling periods were ascribed to enhanced local dust emissions and anthropogenic activities. Aluminum generally comes from the crust due to its abundance in most soils whereas Zn, Pb and Ni may enter the atmosphere through industrial activities and burning of fossil fuel. During the period of 02/04/08–19/05/08 and before, there were a considerable number of soil excavation activities within the college campus, in preparation for construction of a number of buildings such as students' residential, lecture theaters and staff office blocks. This resulted in high Al concentrations due to local dust re-suspension by wind convective processes. Similarly, tear and wear and exhaust emission from machinery used during the excavation processes site also contributed to high concentration levels of Zn, Ni and Pb. Lead, Zn and Ni are often associated with fuel burning (Rhan and Lowenthal, 1984). Additionally, Zn is considered a good marker for tyre wear emissions (Huang *et al*., 1994; Weckwerth, 2001).

Appendix

Dates (DDMMYY)		Metal Concentrations (ng/m^3)								Rain	Wind
Deployed	Removed	Al	Co	Cu	Fe	Mn	Ni	Pb	Zn	mm	m/s
02/04/08	05/04/08	2483.00	0.91	2.07	282.67	8.70	2.58	3.90	1614.49	0.00	16.86
05/04/08	08/04/08	3774.59	0.88	2.89	401.12	13.24	2.14	7.01	1517.73	0.00	15.42
08/04/08	11/04/08	3145.57	1.50	1.91	310.43	10.16	3.05	4.03	1715.71	0.00	21.64
23/04/08	26/04/08	4033.46	1.32	3.53	545.93	19.90	3.19	5.95	2012.26	0.00	21.26
27/04/08	30/04/08	5047.02	1.48	3.48	1043.82	21.31	4.60	5.75	2606.00	0.00	17.38
10/05/08	13/05/08	2847.27	1.44	2.27	271.09	11.44	2.46	5.14	3224.44	0.00	19.25
13/05/08	16/05/08	4565.22	1.22	3.09	500.17	14.37	4.57	8.10	2742.62	0.00	18.44
16/05/08	19/05/08	5354.18	0.62	3.92	568.07	19.76	5.96	9.00	3077.38	0.00	29.53
25/05/08	28/05/08	1248.71	ND	0.94	134.24	7.04	0.92	ND	95.11	3.50	37.22
28/05/08	31/05/08	493.82	ND	3.75	426.12	13.98	1.01	0.44	31.68	0.00	18.47
01/06/08	04/06/08	1115.79	ND	2.33	402.27	12.48	1.42	ND	73.81	5.50	28.58
04/06/08	07/06/08	1371.42	ND	2.86	387.90	12.12	0.82	ND	91.35	0.00	14.32
07/06.08	10/06/08	1362.85	ND	2.68	368.77	12.57	0.72	ND	94.94	0.00	18.30
11/06/08	14/06/08	1115.56	ND	4.21	609.77	17.20	1.03	0.63	64.11	0.00	18.60
14/06/08	17/06/08	1339.96	ND	3.08	725.44	20.58	1.34	ND	80.86	0.00	23.35
17/06/08	20/06/08	1111.57	ND	1.66	508.57	13.49	1.09	ND	75.53	0.00	47.24
20/06/08	23/06/08	1298.05	ND	2.00	447.75	15.04	1.07	0.07	93.45	0.00	28.03
23/06/08	26/06/08	1490.81	ND	5.08	841.32	21.88	1.60	0.18	95.54	0.00	18.38
26/06/08	29/06/08	791.26	ND	3.40	663.12	17.85	1.22	ND	43.49	0.00	14.69
29/06/08	02/07/08	692.06	ND	3.72	572.03	15.53	0.88	ND	42.82	0.00	18.97
02/07/08	05/07/08	848.44	ND	1.79	603.88	18.39	1.15	ND	45.08	0.00	28.02
06/07/08	09/07/08	1123.44	ND	2.68	671.16	19.11	1.16	ND	55.53	0.00	27.51
09/07/08	12/07/08	1029.02	ND	2.54	465.80	15.22	0.88	ND	71.77	0.00	42.85
12/07/08	15/07/08	669.13	ND	2.14	142.74	6.97	0.48	ND	50.06	6.00	39.38
15/07/08	18/07/08	1004.36	1.23	3.99	356.86	14.28	0.77	0.28	76.48	0.00	39.06
18/07/08	21/07/08	1090.90	ND	3.42	510.78	15.16	0.96	ND	82.74	0.00	24.35
21/07/08	24/07/08	1180.97	ND	2.71	512.17	15.64	1.21	0.08	66.50	0.00	25.86
04/08/08	07/08/08	1312.00	ND	4.14	944.80	27.73	1.34	0.09	55.18	0.00	22.38
07/08/08	10/08/08	1114.19	ND	4.69	1163.88	28.20	1.53	ND	44.51	0.00	22.85
10/08/08	13/08/08	1070.68	0.18	2.39	684.19	19.60	1.12	ND	53.46	0.00	21.63
13/08/08	16/08/08	1044.46	ND	1.66	679.81	17.23	0.39	ND	43.38	0.00	37.92
16/08/08	19/08/08	1578.76	ND	1.04	422.14	10.08	ND	ND	77.18	0.00	74.06
19/08/08	22/08/08	1320.90	ND	2.23	454.27	11.64	ND	ND	65.72	0.00	36.47
22/08/08	25/08/08	1184.85	ND	2.70	590.64	13.75	ND	ND	59.56	6.00	32.50
26/08/08	29/08/08	599.25	ND	35.43	637.07	15.85	0.01	ND	21.71	0.00	30.42
29/08/08	01/09/08	1525.47	ND	3.78	814.79	20.30	ND	0.09	53.60	0.00	32.63
01/09/08	04/09/08	696.04	ND	3.04	663.60	18.71	0.14	ND	24.90	1.70	34.78
04/09/08	07/09/08	1837.20	ND	2.98	748.20	20.96	1.47	ND	76.08	0.00	43.19
08/09/08	11/09/08	1572.25	0.20	3.40	823.40	21.42	0.46	ND	68.22	0.00	36.76
11/09/08	14/09/08	1568.19	ND	1.84	357.20	10.26	0.14	ND	51.00	0.00	47.42
15/09/08	18/09/08	1363.02	0.20	3.13	593.86	14.24	0.24	ND	34.88	0.00	45.80
18/09/08	21/09/08	700.17	ND	2.83	486.33	14.48	0.15	ND	13.30	0.00	44.28
21/09/08	24/09/09	1305.41	ND	3.04	644.52	16.40	0.05	ND	23.55	6.00	33.77
24/09/08	27/09/08	2038.99	ND	4.21	37.22	22.58	0.25	ND	36.27	0.00	38.38
27/09/08	30/09/08	2996.07	0.13	2.31	386.33	12.22	0.22	ND	57.05	0.00	64.50
07/10/08	10/10/08	3107.55	ND	2.62	634.12	17.77	0.34	ND	55.18	0.00	47.31
10/10/08	13/10/08	757.10	ND	3.02	608.15	14.77	0.01	ND	27.81	0.00	37.82
13/10/08	16/10/08	2502.41	3.82	2.95	633.04	16.89	1.21	ND	94.66	0.00	49.59
23/10/08	26/10/08	1022.07	4.11	2.05	388.03	9.71	0.93	ND	37.94	6.00	75.73
26/10/08	29/10/08	637.86	0.31	2.19	289.53	7.01	0.03	ND	40.98	0.00	45.77
29/10/08	01/11/08	2154.42	ND	2.65	470.64	12.57	0.07	ND	82.10	0.00	51.29
01/11/08	04/11/08	2203.97	ND	2.59	351.34	10.63	0.59	ND	79.99	5.00	69.30
04/11/08	07/11/08	2131.34	ND	2.66	371.66	10.37	0.28	ND	73.81	4.00	77.26
07/11/08	10/11/08	1805.32	0.96	1.85	119.09	4.69	0.04	ND	68.02	29.50	67.01
10/11/08	13/11/08	2159.48	ND	2.38	141.11	4.82	1.00	ND	78.72	29.70	45.76
13/11/08	16/11/08	2126.56	2.87	2.26	159.28	7.27	0.78	0.51	93.78	18.50	34.39
16/11/08	19/11/08	1516.56	4.29	1.66	135.15	7.06	1.42	ND	85.21	22.50	55.97
19/11/08	22/11/08	1394.34	4.99	1.46	109.63	5.73	1.12	0.22	83.34	9.20	40.37
22/11/08	25/11/08	1057.21	4.11	2.15	165.67	6.62	1.12	0.14	89.16	2.20	25.43
25/11/08	28/11/08	1445.61	5.73	2.56	318.78	10.20	1.60	ND	74.94	0.00	41.70
28/11/08	01/12/08	1335.75	6.25	2.82	271.56	10.87	1.50	0.08	75.49	0.00	49.51
01/12/08	04/12/08	1185.38	4.36	3.99	462.28	13.87	1.76	0.40	78.90	0.00	53.23
04/12/08	07/12/08	1366.15	5.75	1.98	194.39	8.56	1.17	0.13	63.80	24.00	57.27

The geometric mean concentrations of Co, Fe, Ni, Mn, Pb and Zn are within the lower range (**Table 1**) of the annual average guidelines (UK, 2007; WHO, 2000), suggesting very little to no effect of anthropogenic activities on air quality at the site. However, in the assessment of potential effect of the measured metals to air quality at the site, baseline concentrations should be always considered, to obtain a preliminary idea about possible sources of different elements, that is, crustal or anthropogenic. As can be seen from **Fig. 2**, geometric enrichment factors for Al and Zn (EF_g = >>20) are highly enriched suggesting that the metals may have resulted from anthropogenic sources. Park and Dam (2010) reported enhanced levels of Zn concentrations at a sampling station in Korea, which were ascribed to Asian dust coming from highly industrialized zones in China during long-range transport. Al normally represents elements of earth origin. In this study however, highly enriched Al suggest contributions from construction activities, particularly during the sampling period of 02/04/08-19/05/08 (see Appendix). These results are supported by their correlation (r = 0.66; P = 0.01) as shown in **Table 2**, suggesting that the two may have originated from similar sources. Similarly, the highly enriched Co (EF_g = 19) also of correlation coefficients, r = 0.34; P = 0.01 with Al and r = 0.41; P = 0.01 with Zn and moderate enrichments of Cu, Pb and Ni suggests contributions from anthropogenic sources. This analysis will however be clarified further by principal component analysis which will be explained later in this discussion. As expected, significant negative correlations of rainfall (P = 0.01) with Cu, Fe and Mn are a result of washout of atmospheric particles by rainfall which also tends to reduced re-suspension of crustal dust. Similarly, significant negative correlations of wind speed (P = 0.01) with Cu, Fe, Mn, Ni and Pb suggest high dispersion conditions leading to lower aerosol concentrations. On the other hand, Al, Co, Ni, Pb and Zn show insignificant correlations with rainfall amount. Although this was unexpected, this may suggest that these elements occur in significantly different aerodynamic diameters, resulting in different settling times or washout ratios. Insignificant correlations between wind speed and Al, Co and Zn however suggest that these elements are probably originating from both local and distant sources.

Interpretation of results from correlation analysis was not easy and therefore was supplemented by principal component analysis in which particle data was calculated to find special coexistence and separate existence of elements. From FA-1, PC-1 was characterized by Pb, Zn Ni and Al and PC-2 by Fe and Mn. PC-1 supports observed correlations depicted in **Table 2**. Thus, on the basis of these observations and the corresponding moderate to high EF_g values (**Fig. 2**), Pb, Zn Ni and Al exist possibly because of anthropogenic contributions. Fossil fuel combustion, traffic emissions, wear of break lining materials and several industrial processes are considered as major sources of Pb, Zn and Ni (Al-Momani, 2009). Although elevated EF_g values of Al were unexpected, its presence in elevated forms and association with Pb, Zn and Ni could be attributed to industrial activities during construction. PC-2 (**Fig. 3**) was characterized by Fe and Mn. This supports the high correlation (r = 0.86; P = 0.01) between these metals (**Table 2**). The natural sources of Fe (~98%) vastly dominate its anthropogenic input (Tippie, 1984), thus, Fe and Mn probably indicate soil mineral particles. The enrichment value of unity for Mn (taking into account that Fe was used for reference material) further suggests crustal origin of both metals, such as the airborne dust.

On the other hand, the second factor analysis (FA-2) revealed three component factors which were comprised of 91% total cumulative variance. PC-1 was characterized by Cu, Fe and Mn (**Table 4**). Since Fe and Mn are tracers for natural sources and this PC has strong communalities of 0.999 and 0.962, respectively, it indicates the association of Cu, Fe and Mn with crustal sources. From the previous discussion, moderate EFs values (**Fig. 2**) reported for Cu, Pb and Zn were suggested to be associated with contributions from anthropogenic sources. In this regard, the possibility of Cu resulting from both lithogenic and anthropogenic sources cannot be ruled out. However, according to results obtained from FA-1 (**Table 3**), Cu had insignificant factor loadings in PC-1 but relatively weak loadings in PC-2 (elements which are characterized as either lithogenic or anthropogenic), whereas, in FA-2, Cu was strongly associated with the lithogenic Fe and Mn. These findings suggest that existence of copper in the measured aerosol samples in Gaborone is almost entirely due to lithogenic sources.

The second Principal Component (PC-2) was characterized by Pb, Al and Zn, which was ascribed to local anthropogenic sources. Since the sampling station was a few hundred metres away from the only highway connecting the city of Gaborone with the northern part of the country, high levels of Pb in air sample might be associated with fossil fuel consumption, whereas Zn could be a result of wear and tear of vulcanized rubber

tyres, lubricating oils and corrosion of galvanized vehicular parts. As discussed before, the presence of Al in PC-2 is a result of emission from the local construction activity during the sampling period. Lastly, PC-3 was characterized by Co and Ni. Ni is commonly associated with emissions from industries such as electroplating, ferrous and non-ferrous foundries (Kulshrestha *et al*., 1995). It was however difficult to associate the presence of Co and Ni with such industrial activities since the authors could not identify such industries within the sampling vicinity. In that case, interpretation of these results will be discussed in conjunction with findings from back-trajectory analysis.

The HYSPLIT model was run to generate 72-h back trajectories arriving at the sampling site to identify potential source regions. Measured metal concentration data for each element were analysed in conjunction with their corresponding trajectories. Only Zn and Ni mean concentrations (**Table 5**) were found to exhibit geographical dependence as shown in **Fig. 5**. Trajectories in CL 2 carry aerosol particles which are relatively rich ($P < 0.5$) in Zn atoms compared to trajectory clusters 4 and 5. However, they do not exhibit significant differences in Zn mean concentrations between CL 1 and CL 3. Trajectory clusters 2 and 3 are slow-moving and continental. Air masses with high residence times over the continent and slow moving will tend to acquire characteristics distinctive to the land they are ambient to. Therefore, enhanced Zn concentrations associated with these air masses are results of industrial activities along the southern belt (CL 2) of Botswana and those that are along the eastern sides of Botswana (CL 3). Trajectory CL 1 is also along CL 3, but fast moving, with 1/3 of its entire time over the ocean before reaching the sampling station. It is expected that CL 1 be similar to CL 3, but slightly diluted by the oceanic clean air, as can be depicted from results in **Table 5**. A similar argument holds for observations made with Ni mean concentrations in clusters 1, 2 and 3, which are significantly ($p<0.5$) high compared to Ni concentrations in cluster 4.

Further to the above, air mass trajectories provide information as to whether metal concentrations obtained from the study are local pollutant or transported from elsewhere, with the possibility of being trans-boundary. As discussed previously, the presence of Ni and possibly Co in the aerosol samples measured in the study could possibly be due to both local and trans-boundary contributions.

5. CONCLUSION

In general, different metals (Al, Zn, Pb and Ni) showed different patterns of air concentrations in the sampling periods 02/04/08-19/05/08 and 13/11/08-07/12/08. This was ascribed to the excavation activities that took place during the first part of the sampling period which introduced high concentrations of dust particles as compared to the latter part. Cu, Fe and Mn, however showed no observable pattern in mean concentrations throughout the sampling periods.

Correlations between Cu, Fe, Mn, Ni and Pb and rainfall and wind speed were observed. However, no significant correlations were observed between rainfall and Al, Co, Ni, Pb and Zn. Similarly, there were no significant correlations between wind speed and Al, Co and Zn. A large number of data set is needed to improve statistical significance for correlation analysis to be successful.

Factor analysis reveals that Pb, Ni, Co, Al and Zn exist because of anthropogenic contributions, whereas, Fe and Mn are from lithogenic sources. On the other hand, Cu exists from mixed sources.

Back-trajectories were used to locate geographical potential source regions of heavy metals. The presence of Zn and Ni in the aerosols measured at Sebele is due to air mass transportation processes.

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