Identification of sources of aerosol particles in three locations in eastern Botswana

S. Chimidza and K. Moloi

Environmental Physics Department, Chalmers University of Technology–University of Gothenburg Gothenburg, Sweden Department of Physics, University of Botswana, Gaborone

Abstract. Airborne particles have been collected using a dichotomous virtual impactor at three different locations in the eastern part of Botswana: Serowe, Selibe-Phikwe, and Francistown. The particles were separated into two fractions (fine and coarse). Sampling at the three locations was done consecutively during the months of July and August, which are usually dry and stable. The sampling time for each sample was 12 hours during the day. For elemental composition, energy-dispersive x-ray fluorescence technique was used. Correlations and principal component analysis with varimax rotation were used to identify major sources of aerosol particles. In all the three places, soil was found to be the main source of aerosol particles. A copper-nickel mine and smelter at Selibe-Phikwe was found to be not only a source of copper and nickel particles in Selibe-Phikwe but also a source of these particles in far places like Serowe. In Selibe-Phikwe and Francistown, car exhaust was found to be the major source of fine particles of lead and bromine.

1. Introduction

Several studies have shown that atmospheric aerosol particles can have impact on climate as well as on human health. Particulate matter contributes significantly to radiative forcing of climate [Andreae, 1996; Sokolik and Toon, 1996; Langmann et al., 1998], and some health effects have, for instance, recently been elaborated on by Sarangapani and Wexler [1998], Hornberg et al. [1998], and Hadnagy et al. [1998].

In order to have good model predictions of radiative forcing due to particulate matter, characterization of aerosol particles in many different locations is essential. Implementation of appropriate countermeasures against health risks, estimation of local and regional concentrations of aerosol particles, and identification of pollution sources are also issues of importance that call for aerosol characterization.

Characterization of aerosol particles is very important in the Southern Hemisphere, where only a few measurement data are available [Maenhaut and Akilimali, 1987; Kent et al., 1998]. In Botswana (22°S, 24°E), only recently has an attempt to quantify elemental concentrations of aerosol particles been made [Selin Lindgren et al., 1999]. In this paper, trace element concentrations in airborne particulates at three different locations in Botswana are presented, and possible sources are identified. A dichotomous virtual impactor and energy-dispersive x-ray fluorescence (EDXRF) technique were used for sample collection and analysis, respectively.

2. Experiment

2.1. Sampling

Airborne particulates were sampled at three different places in Botswana: Serowe, Selibe-Phikwe, and Francistown (Figure 1). Serowe, with a population estimated at 55,000, is one of the

Copyright 2000 by the American Geophysical Union.

Paper number 2000JD900182. 0148-0227/00/2000JD900182**\$**09.00 large traditional villages in Botswana. With the exception of emissions from sparse traffic and wood, used by most house-holds as a domestic energy source, the anthropogenic sources of pollution in Serowe are very few. However, the village is situated ~ 40 km NW of a coal mine and a large coal-powered station located at a place called Morupule. Selibe-Phikwe is a small mining town ~ 150 km NE of Serowe and has a population of $\sim 46,000$. There is a copper-nickel mine and smelter in this town, and traffic is moderate. Francistown is the second largest city in Botswana and has a population of $\sim 78,000$. Traffic in this city is dense, and there are quite a number of industries.

In all the three sampling places the sampling instrument was placed ~ 1 m above ground level. The sampling site in Serowe was a residential place inside a secondary school yard. The school is in the eastern part of the village and is built close to a small hill (<10 m high). In Selibe-Phikwe the sampling site was in a military camp ~ 1 km from the city center. The site is approximately 300 m from a copper-nickel mine and smelter. In Francistown a residential place inside a secondary school yard was used for sampling. The school is ~ 1 km north of the city center.

The sampling instrument is composed of a pump and a dichotomous virtual impactor. The pump, which is fitted with a control module for the total and the coarse particle flow, draws the air through the impactor at a total flow rate of $1 \text{ m}^3/\text{h}$. Two types of impactors were used in this work. The two impactors differed in both the upper cutoff aerodynamic diameters and the two size ranges into which the impactor segregates particles. The two size ranges will hereafter be referred to as the coarse (c) and fine (f) fraction/particles. In Serowe the size ranges were 3.5–18 μ m and <3.5 μ m, while in Selibe-Phikwe and Francistown the ranges were 2.5–10 μ m and <2.5 μ m for coarse and fine fractions, respectively. The two impactors are usually referred to as PM-18 and PM-10 to signify their upper cutoff points. As elaborated on by Foltescu and Selin [1993], this difference in cutoff points may be significant and needs to be taken into account when comparing data from two different



Figure 1. Map of Botswana with the different sampling places shown. Sampling places used in this work and those used in the work previously reported by *Selin Lindgren et al.* [1999] are shown. Serowe and Francistown are used in the present work while Gaborone and Palapye were used in the previous work. Selibe-Phikwe was a sampling site in both.

dichotomous impactors. However, for the elements for which the fine particle fraction dominates, the difference in impactor cutoffs will have an influence of <10% when comparing results of the fine particle aerosol [*Foltescu and Selin*, 1993]. Fine particles are mainly a result of gas to particle conversion or are formed at high temperatures.

Aerosol particles were collected on Teflon membrane filters

of diameter 29 mm. Filters were mounted in pairs to collect fine and coarse particles in the respective channels of the impactor. For security reasons, sampling time for each pair of filters was ~12 hours during the day. Sampling was done during the months of July and August 1998. The meteorological conditions during this period were very stable with no rainfall, and most of the days were clear and sunny with low wind speeds (<2 m/s). The total number of filter pairs collected at each of the three sampling places are 14, 15, and 16 for Serowe, Selibe-Phikwe, and Francistown, respectively. At Serowe, 8 filter pairs were collected from July 5 to 12, and 6 pairs were collected from July 23 to 28. Collection at Selibe-Phikwe was done from July 29 to August 12, while at Francistown the 16 filter pairs were collected from August 13 to 28.

2.2. Analytical Technique

Aerosol filter samples were analyzed using energy-dispersive x-ray fluorescence (EDXRF) technique. The spectrometer used has a three-axial geometry setup described in more detail by *Standzenieks and Selin* [1979] and *Selin et al.* [1991]. This geometry minimizes the background radiation such that low detection limits are achievable. Figure 2 shows a typical spectrum from an EDXRF analysis. From left to right, the elements are displayed in order of increasing x-ray energy. The two large peaks to the far right end of the spectrum show the inelastically and elastically scattered K- α and K- β radiation from the secondary molybdenum target. In this case the range of analysis for the spectrometer is from silicon to lead.

The basic input data are obtained from the analysis of a spectrum like that shown in Figure 2. The software package program, Analysis of X-ray Spectra by Iterative Least Squares Fitting (Axil), was used to evaluate the areas under the peaks [Van Espen et al., 1986]. In the calculation of concentrations the program uses an equation of the form

$$m_i = \frac{I_i}{k_i C_i} \tag{1}$$

where



Figure 2. A typical aerosol spectrum of coarse and fine particles from an EDXRF analysis. Characteristic lines, which are marked by their respective elements, and the background under the characteristic lines are shown. With the exception of lead, for which L- α and L- β radiation are displayed, K x rays are displayed for all elements. The channel number is linearly proportional to the x-ray energy.

- m_i areal density, $\mu g/cm^2$;
- I_{i} intensity of characteristic line, counts per second (cps);
- C_i attenuation correction factor;
- k_i sensitivity factor, cps cm² μ g⁻¹.

Using information on the area of the filter and the volume of air sampled, the areal densities ($\mu g/cm^2$) are converted to air concentrations (ng/m^3). A correction was also made for the small fraction of fine particles that is collected on the coarse filter. Statistical analysis of data was made using other complementary programs such as Statistica [*StatSoft*, 1994].

2.3. Detection Limits for EDXRF Analysis of Aerosol Filters

Sensitivity of x-ray spectrometric analysis is usually defined in terms of the minimum detection limit. This is the concentration level above which it is possible to say with reasonable certainty that the element is present. The most widely accepted definition of minimum detection limit is the amount of analyte that gives a net line intensity equal to 3 times the square root of the background intensity for a specified counting time [*Bertin*, 1975]. This gives a confidence level of 99.7%. The detection limits for the EDXRF spectrometer used in this study are shown in Table 1.

3. Results and Analysis

3.1. Means, Medians, and Interquartile Ranges

A summary of the results obtained from the EDXRF analvsis is shown in Table 2. Seventeen elements ranging from silicon to lead are shown. Some elements which were below detection limit, but within the range of the analysis, are not shown in the table. Three parameters are shown: mean, median, and interquartile range. The median is given since a few outlier values will have a great effect on the mean while the median values are not influenced by extremes and thus may be a better indication of the typical concentration of the element [Helsel, 1990]. However, the mean concentration during even a short period represents the actual average concentration in the air during that period. Thus, if the concern is to measure deposition of air pollution, then the mean concentration is the appropriate value to use. The interquartile range (IQR) is given to indicate the spread of the values. By definition the IQR is the difference between 75th percentile and the 25th percentile and thus is the range of the central 50% of the data. Like the median, the IQR is not affected by a few outlier values.

For most of the elements the mean is greater than the median. This shows that the data contain a few high outliers. Soil-derived elements depict a very high IQR which shows that the values have a large spread. Thus the concentration from one day to another differs markedly.

The IQRs for fine particle concentrations of bromine and lead, which are characteristic for exhaust from leaded petrol, for Selibe-Phikwe and Francistown are high compared to those for Serowe. This could be explained by the fact that in Selibe-Phikwe and Francistown there is more traffic during working days than during weekends while in Serowe, a rural village, traffic is almost the same throughout the week. A large difference in traffic intensity will give a large difference in emissions of lead and bromine, which, in turn, gives a large IQR. For both lead and bromine the fine particles dominate, and there-

Table 1. Detection Limits for Quantification of Elements
in Airborne Particles Analyzed With EDXRF Technique
From a Measurement Using Teflon Filters

Element	Detection Limit,* ng/cm ²	Minimum Airborne Concentration,† ng/m ³		
Si	1400	720		
S	90	46		
Cl	40	21		
K	15	7.7		
Ca	8.0	4.1		
Ti	5.1	2.6		
v	2.8	1.4		
Cr	2.1	1.1		
Mn	2.5	1.3		
Fe	1.3	0.67		
Ni	1.2	0.62		
Cu	0.95	0.49		
Zn	0.89	0.46		
Br	0.62	0.32		
Rb	0.54	0.28		
Sr	0.63	0.32		
Pb	0.92	0.47		

*Detection limits are calculated using the 3 times square root of background (3σ) . The time of spectrum acquisition considered is 1000 s.

†The minimum airborne elemental concentrations are calculated with respect to the 12 hours sampling time used in this study.

fore the difference in cutoff points is not expected to be significant.

From Table 2 it can be observed that the Botswana aerosol is a typical arid climate aerosol which is rich in coarse soilderived elements: silicon, iron, titanium, calcium, potassium, manganese, rubidium, and strontium. When comparing concentrations of these elements in Botswana with measurements done in Scandinavia [*Foltescu et al.*, 1994, 1996; S. Chimidza and K. Moloi, unpublished data, 1997], it is evident that the levels of titanium and iron are approximately 50–100 times higher in Botswana, and those of potassium, rubidium, manganese, strontium, and calcium are 10–30 times higher in Botswana. Generally, Selibe-Phikwe shows a higher concentration of soil-derived elements compared to the other two sites. This enhancement can be due to additional soil elements from the copper-nickel ore.

Serowe shows a high fine particle concentration of sulfur even though it is a rural village. The fine particle sulfur concentration in Serowe is more than double the concentrations at the other two places while the coarse particle sulfur concentrations at all the three places are below detection limit. The high concentration in Serowe could be due to Serowe's downwind location with respect to the Morupule coal-powered station and the Selibe-Phikwe copper-nickel mine and smelter. On average, Botswana experiences easterly winds throughout the year [Bhalotra, 1987]. Thus Serowe is subjected to mostly easterly winds which have gone through Morupule or Selibe-Phikwe. Sulfur is emitted as sulfur dioxide (SO_2) and converted to fine particulate sulfate at an approximate rate of one or a few percent per hour [Seinfeld, 1986; Finlayson-Pitts and Pitts, 1986]. Thus one expects to find less particulate sulfate at the source than far away from it, particularly if there is little dispersion of the plume and a constant wind drift carries away the SO_2 from the source.

ElementMeanMedianIQRMeanMedianIQRMeanMedianSi(c)49004700170078008000300039003900Si(f)BDLBDLBDLBDLBDLBDLBDLBDLBDLS(c)BDLBDLBDLBDLBDLBDLBDLBDLS(c)210130140310310250230100Cl(c)210130140310310250230100Cl(f)10060418063507762K(c)290290100840920280350340K(f)450390370250250200320290Ca(c)240022002000830920280690620Ca(f)160170567767505544Ti(c)1601508824027084110110Ti(f)15155.72218188.07.1V(c)6.97.64.68.08.64.04.03.9V(f)BDLBDLBDLBDLBDLBDLBDLBDLMn(c)4750285560192825Mn(f)6.06.33.45.95.15.12.82.6Fe(Serowe			Selibe-Phikwe			Francistown		
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Element	Mean	Median	IQR	Mean	Median	IQR	Mean	Median	IQR
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Si(c)	4900	4700	1700	7800	8000	3000	3900	3900	250
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Si(f)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S(c)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	S(f)	960	1100	660	320	280	260	320	320	330
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cl(c)	210	130	140	310	310	250	230	100	230
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cl(f)	100	60	41	80	63	50	77	62	28
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	K(c)	290	290	100	840	920	280	350	340	210
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	K(f)	450	390	370	250	250	200	320	290	220
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ca(c)	2400	2200	2000	830	920	280	690	620	350
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ca(f)	160	170	56	77	67	50	55	44	33
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ti(c)	160	150	88	240	270	84	110	110	80
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Ti(f)	15	15	5.7	22	18	18	8.0	7.1	5.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	V(c)	6.9	7.6	4.6	8.0	8.6	4.0	4.0	3.9	2.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	V(f)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cr(c)	7.2	6.1	4.6	7.4	9.1	3.0	3.3	3.3	3.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cr(f)	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mn(c)	47	50	28	55	60	19	28	25	15
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Mn(f)	6.0	6.3	3.4	5.9	5.1	5.1	2.8	2.6	1.3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Fe(c)	2100	1900	990	3100	3400	1000	1300	1300	770
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Fe(f)	210	210	50	320	260	210	110	100	86
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni(c)	6.1	5.0	3.0	23	22	7.7	4.9	3.5	4.2
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Ni(f)	1.8	1.7	1.1	3.3	2.3	1.7	0.8	0.6	0.6
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu(c)	7.8	6.2	3.2	22	21	5.1	5.4	5.0	4.3
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Cu(f)	3.1	2.3	1.7	3.1	2.3	2.0	1.3	1.1	0.1
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Zn(c)	10	8.4	7.9	13	14	5.2	6.9	6.5	5.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Zn(f)	6.1	6.8	1.7	4.1	3.4	3.1	4.4	3.7	2.8
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Br(c)	1.1	0.8	0.5	4.9	1.7	1.3	1.9	1.5	1.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Br(f)	7.6	8.0	1.1	12	8.5	6.8	9.1	8.3	6.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Rb(c)	1.4	1.4	0.4	5.3	5.6	1.8	1.9	2.0	1.0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Rb(f)	0.9	0.7	0.6	0.8	1.1	0.7	0.6	0.6	0.4
Sr(f) 1.0 1.1 0.6 0.7 0.6 0.0 0.4 0.3 Pb(c) 3.6 3.5 0.7 15 5.8 2.7 5.6 4.0 Pb(f) 9.5 8.0 3.4 22 8.5 13 11 6.3	Sr(c)	7.5	6.6	4.5	7.6	8.2	2.6	4.5	4.3	2.2
Pb(c) 3.6 3.5 0.7 15 5.8 2.7 5.6 4.0 Pb(f) 9.5 8.0 3.4 22 8.5 13 11 6.3	Sr(f)	1.0	1.1	0.6	0.7	0.6	0.0	0.4	0.3	0.3
Pb(f) 9.5 8.0 3.4 22 8.5 13 11 6.3	Pb(c)	3.6	3.5	0.7	15	5.8	2.7	5.6	4.0	5.3
	Pb(f)	9.5	8.0	3.4	22	8.5	13	11	6.3	11

 Table 2.
 Means, Medians, and Interquartile Ranges for Selected Elements in the Three Locations

The notation BDL means below detection limit; IQR, interquartile ranges. Concentrations are in ng/m³.

3.2. Time Series of the Elements

Time series of selected elements are shown in Figures 3 and 4. It is worthwhile mentioning that both modes of particles show some variation from one day to another. This could be an indication that the daily concentrations are dependent on the meteorological parameters such as the wind direction. The measured elemental concentrations of elements that are emitted by a localized source may be high or low dependent on the wind direction. Figure 3 shows the similarity in the variations of Fe(c) and Si(c) in Serowe, while Figure 4 shows the same for



Figure 3. Time series of silicon(c) and iron(c) at Serowe. Both silicon(c) and iron(c) are soil derived. Correlation coefficient r = 0.98.



Figure 4. Time series of copper and nickel at Selibe-Phikwe, which has a copper-nickel mine and smelter. Correlation coefficient r = 1.00.

Table 3.	Correlation	1 Coefficients	From Principal
Componen	nt Analysis i	for the Three	Sites

Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Si(c) 0.946	Ni(c) 0.897	Serowe	S(f) 0.880	Cl(c) 0.900
Ca(c) 0.946 Ca(c) 0.943 Ti(c) 0.969	Ni(f) 0.948		Zn(f) 0.742	Cl(f) 0.868
V(c) 0.891 Cr(c) 0.830	Cu(c) 0.931		Rb(f) 0.704	Br(c) 0.922
Mn(c) 0.955 Fe(c) 0.963 Zn(c) 0.962 Rb(c) 0.814 Sr(c) 0.967	Cu(f) 0.857		K(f) 0.622*	
		Saliba Dhilana		
Si(a) 0.840	Co(f) 0 724	Sellbe-Frikwe		
K(c) 0.874	Ti(f) 0.827	3(1) 0.047		
Ca(c) 0.913 T ₁ (c) 0.917	Mn(f) 0.727 Fe(f) 0.852	Br(c) 0.967		
V(c) 0.854	Ni(c) 0.806	Br(f) 0.951		
Mn(c) 0.925 Fe(c) 0.881	Cu(c) 0.938 Cu(c) 0.807 Cu(f) 0.939	Pb(c) 0.966		
Zn(c) 0.873 Rb(c) 0.868 Sr(c) 0.915	Sr(f) 0.893	Pb(f) 0.959		
		Francistown		
Si(c) 0.902 K(c) 0.897		Zn(f) 0.702	S(f) 0.888	
Ca(c) 0.857 Ca(f) 0.830		Br(c) 0.854	K(f) 0.878	
Ti(c) 0.932		Br(f) 0.781	Rb(f) 0.867	
V(c) 0.877		Pb(f) 0.706		
Cr(c) 0.716 Mn(c) 0.038				
Mn(c) 0.938 Mn(f) 0.906				
Fe(c) 0.939				
Fe(f) 0.887				
Zn(c) 0.849				
Rb(c) 0.907				
Sr(c) 0.874				

*With the exception of this coefficient the tabulated correlation coefficients are greater than 0.7.

Ni(c) and Cu(c) in Selibe-Phikwe. This is an indication that like Fe(c) and Si(c) in Serowe, Cu(c) and Ni(c) in Selibe-Phikwe have a common source. The concentration levels of each pair of elements show very high correlation coefficients (see Figures 3 and 4).

3.3. Correlations and Factor Analysis

In order to identify the major aerosol sources and to apportion the various elements to these sources, the data were subjected to correlations and principal component analysis (PCA) [StatSoft, 1994] with varimax rotation. The correlations of a few selected elements with respective factors are shown in Table 3. It is worth noting that the elements which are highly correlated to the same factor are, in turn, highly correlated to each other. Factors are arranged such that the source attributed to the factor is the same irrespective of the place. For Serowe and Francistown the factors shown represent $\sim 73\%$ of the analyzed element fractions, while for Selibe-Phikwe, approximately 83% are represented.

With a very few exceptions in Francistown, the first factor consists of coarse particles. For this reason, the factor is attributed to soil. Coarse particles are composed mainly of mechanically generated particles and resuspended soil particles [Hinds, 1982]. Furthermore, the factor comprises elements for which the main source is known to be soil (Si(c), Fe(c), Ca(c), K(c), and Rb(c)). At each of the three places this factor comprises the largest percentage of the element fractions apportioned to the different factors (68%, 50%, and 44% for Francistown, Serowe, and Selibe-Phikwe, respectively).

Factor 2 is only represented at two places, Serowe and Selibe-Phikwe. Approximately 36% of the apportioned element fractions in Selibe-Phikwe and $\sim 18\%$ for Serowe belong to this factor. In Serowe the only elements correlated to this factor are nickel and copper, in both coarse and fine fractions, while in Selibe-Phikwe there are a few additional elements in the fine fraction. The concentrations of both copper and nickel at Serowe are less than the concentrations in Selibe-Phikwe, and the ratios of fine to coarse for the two elements are higher in Serowe (0.4 and 0.3 for copper and nickel, respectively, in Serowe, compared to 0.1 for both elements in Selibe-Phikwe).



Figure 5. Scattergram of bromine(f) versus lead(f) for Francistown. The confidence level is 95%. The slope of the regression line gives the bromine to lead ratio.

This is an indication that the source of copper and nickel found in Serowe is the Selibe-Phikwe copper and nickel mine and smelter. Because of a relatively higher deposition rate for the coarse particles, the aerosol size distribution is shifted toward the fine particle region during transport in the atmosphere. This would result in an increase in the ratio of fine to coarse particles as the air parcel moves away from the source. However, because of the difference in impactor cutoff points, the fine to coarse ratio in Serowe may be slightly different from what would have been measured with the PM-10 impactor. In Selibe-Phikwe, the additional fine elements in factor 2 (Table 3) could be from the copper-nickel ore. The reason why these additional elements do not correlate with copper and nickel in Serowe can be that there are other sources of appreciable amounts of these elements in Serowe.

Among other elements, bromine(f) and lead(f) are correlated to factor 3. This factor is only represented in Francistown and Selibe-Phikwe. The factor comprises $\sim 18\%$ and $\sim 20\%$ of the apportioned element fractions in Francistown and Selibe-Phikwe, respectively. In countries where leaded petrol is still in use, the bromine(f) to lead(f) ratio is usually used as an indicator of vehicle exhaust [Faiq and Al-Taie, 1988; Harrison and Sturges, 1983; Liu et al., 1995]. In Botswana, only recently has unleaded petrol been introduced, and thus an appreciable number of vehicles still use leaded petrol. The bromine to lead ratio was therefore used to check if the source for this factor could be vehicle emissions. A ratio of 0.47 with coefficients 0.90 and 0.94 was obtained for Francistown and Selibe-Phikwe, respectively (Figure 5 illustrates the bromine-lead correlation for Francistown). The ratios are in good agreement with both the bromine to lead ratio for the capital city of Botswana reported in previous work [Moloi et al., 1998] and the leaded petrol theoretical ratio of 0.45 (Shell South Africa, personal communication, 1998).

The elements in factor 4 could come from more than one source. Sulfur(f), zinc(f), rubidium(f), and potassium(f), which are in factor 4, could result from both coal combustion [*Clarke and Sloss*, 1992; *Tillman*, 1994] and biomass burning [*Gaudichet et al.*, 1995]. However, with the relatively high concentrations of sulfur at Serowe the most probable source for this

factor at Serowe is coal combustion at Morupule. Furthermore, because of the fact that the factor contains only fine particulates the most likely source is considered to be coal combustion. Fine particles are generally more significant in high-temperature processes. During the measurement period no large-scale biomass burning was reported within an appreciable distance from the measurement sites. The only contribution from biomass burning could have been emissions from the household wood fires. However, this contribution is not expected to be significant as the samples were collected during the day, when wood fires are minimal. Therefore it is most likely that the source for this factor in Francistown is also coal combustion. Most small industries in Francistown use coal combustion as a source of energy. The factor contributes $\sim 18\%$ of the apportioned element fractions in Serowe while in Francistown it contributes approximately 14%.

Factor 5 is only represented at Serowe, and it consists of Cl(c), Cl(f), and Br(c). The major contributor of these elements is usually sea salt. However, with Serowe being very far from the sea it is quite unlikely that the source of Cl(c) and Br(c) is sea salt. One other possible source which is known to contain chlorine and bromine is coal [Davidson, 1996; Harrison and Sturges, 1983]. This source is also unlikely since coal usually contains an appreciable amount of sulfur and sulfur is not correlated to factor 5. Although biomass burning is known to emit halogen-containing compounds [Seinfeld and Pandis, 1998; Lobert et al., 1999], it is difficult to attribute the factor to biomass burning as no lucid fingerprints for biomass burning are contained in this factor. It is concluded that the source for this factor is not known.

3.4. Comparison With Measurements Made During 1997

In Table 4 the measurements from the present campaign are compared with the previous measurements made in 1997 [Selin Lindgren et al., 1999]. The values shown in Table 4 are the sum of median concentrations (coarse plus fine). It is noteworthy that the EDXRF spectrometer used in 1997 had higher detection limits than the one used in the present measurement. This is the main reason why it was then not possible to detect vanadium and chromium. Overall it can be seen that the

	1997			1998			
Element	Gaborone*	Palapye*	Selibe-Phikwe*	Serowe*	Selibe-Phikwe†	Francistown [†]	
Si	5000	8500	6800	5500	8900	4500	
S	1200	920	1000	1200	420	380	
Cl	350	460	450	190	370	160	
Κ	1200	1500	590	680	1200	630	
Ca	910	1800	460	2400	1000	660	
Ti	230	330	130	170	290	120	
V	BDL	BDL	BDL	9.0	9.0	5.0	
Cr	BDL	BDL	BDL	8.0	10.0	4.0	
Mn	65	98	46	56	65	28	
Fe	2800	4200	1100	2100	3700	1400	
Ni	BDL	BDL	47	7.0	24	4.0	
Cu	16	15	29	8.0	24	6.0	
Zn	41	29	17	15	17	10	
Br	120	36	16	9.0	10	10	
Rb	15	14	7.0	2.0	7.0	3.0	
Sr	8.0	17	8.0	8.0	9.0	5.0	
Pb	250	49	28	12	14	10	

 Table 4.
 Comparison of Median Concentrations (Sum of Coarse and Fine Particles) of the Present Measurement (1998) to the Previous One Done in 1997 [Selin Lindgren et al., 1999]

BDL means below detection limit. Concentrations are in ng/m³.

*Upper impactor cutoff is $\leq 18 \ \mu m$.

†Upper impactor cutoff is $\leq 10 \ \mu m$.

present measurements are similar in magnitude to the previous ones. Occasional large differences can be due to the prevailing meteorological conditions like wind and precipitation. For example, the low values of coarse soil-derived elements in Selibe-Phikwe during the 1997 campaign can be attributed to rain washout since it was raining at Selibe-Phikwe when the measurement campaign was in progress. The measurement system can thus be used for further measurements in other locations in Botswana with a possibility of comparison between measurements done in different years. The 1997 and 1998 campaigns are regarded as the first steps in a long-term study.

4. Discussion and Conclusions

Measurements of levels of fine and coarse aerosol particles in three locations in eastern Botswana are reported in this work. One of the three locations has been studied before [Selin Lindgren et al., 1999] and hence provides a basis for comparison of measurements done in two different years. From the comparison of the measurements the measurement technique has proven to give consistent results. As a consequence of this, further measurements in other locations in Botswana can be conducted in the near future, resulting in improvement in the overall information on contributions to aerosol particles from natural as well as anthropogenic sources in Botswana. In view of the difficulty in correcting for use of impactors with different cutoff points, future measurements should use similar impactors, namely PM-10. Inclusion of size distribution measurements could also be a great step in characterization of aerosols in Botswana.

Using factor and regression analysis, natural and anthropogenic sources of aerosol particles at the three locations have been identified. As an example, it can be mentioned that the copper-nickel mine and smelter in Selibe-Phikwe has an impact in the air quality of both Selibe-Phikwe and Serowe, located ~ 150 km away. This is demonstrated by raised concentration levels of both size modes of Cu and Ni in both Selibe-Phikwe and Serowe. The coarse particle concentrations of soil-derived elements are significantly larger than those measured in Scandinavian countries (10–100 times). Thus the elemental fluxes in Botswana are expected to be 1 or 2 orders of magnitude larger than in Scandinavian countries. There is a need for accurate calculations of elemental fluxes in Botswana. The calculations have to be based on meteorological parameters and on measurements of concentrations as well as of deposition velocities.

Although coal combustion has been pointed out as a possible source of some fine particulates in both Francistown and Serowe, there is need for characterization of elements from coal combustion from the Morupule power station at distances closer to the source. A combination of such a study with measurement of gases such as SO_2 and characterization of elements from the coal ash may shed light on the source(s) of some elements measured in Serowe.

No factor in this measurement has been attributed to biomass burning despite the fact that biomass burning is common in developing countries. This is most probably attributable to the restriction in sampling time. In Botswana, fires are more prevalent in the mornings and evenings when most of the cooking and space heating are done. Since the samples were only collected during the day, when biomass burning is minimal, the contribution of biomass burning to the aerosol particles in Botswana is not apparent. There is therefore need for more studies including biomass emissions. This is even more important considering the fact that black carbon from biomass burning plays an important role in attenuation of solar radiation. Measurement of black carbon size-segregated aerosol would be a valuable asset in climate modeling.

The levels of fine particulate lead and sulfur are high in spite of the relative low level of industrialization. There is therefore need for more strict air pollution control before Botswana becomes heavily industrialized. Notwithstanding the government effort to encourage use of unleaded petrol throughout the whole country, a more stringent policy aimed at total extermination of use of leaded petrol in the not distant future should be worked out. This would help in reducing levels of fine particulate lead.

While the measurements discussed in this work covered only two months, it is believed that they give an estimate of the concentration levels found at the three locations. Since the measurements were made during a dry period characterized by low wind speeds, it is possible that the mean concentrations calculated from measurements made during a whole year are smaller than the quoted mean concentrations. Nonetheless, since the measurements were done during a period with the most common type of weather in Botswana, the deviation from the quoted means and medians is not expected to be large.

Acknowledgments. The authors are appreciative of the financial support of SIDA and the University of Botswana. We are also grateful for the technical and other assistance from Jan Jacobsson, Paulis Standzenieks, Eva Selin Lindgren, and Mats Oblad.

References

- Andreae, M. O., Raising dust in the greenhouse, *Nature*, 380, 389–390, 1996.
- Bertin, E. P., Principles and Practice of X-ray Spectrometric Analysis, 2nd ed., p. 529, Plenum, New York, 1975.
- Bhalotra, Y. P. R., Climate of Botswana, Dep. of Meteorol. Serv., Minist. of Works and Commun., Gaborone, Botswana, 1987.
- Clarke, L. B., and L. L. Sloss, Trace elements: Emissions from coal combustion and gasification, *Rep. ICTIS/TR IEA Coal Res.*, 49, 13– 33, 1992.
- Davidson, R. M., Chlorine and other halogens in coal, Rep. ICTIS/TR IEA Coal Res. Perspect., 28, 3-17, 1996.
- Faiq, S. Y., and F. A. Al-Taie, Atmospheric lead and bromine levels in downtown Baghdad, Water Air Soil Pollut., 42, 153–158, 1988.
- Finlayson-Pitts, B. J., and J. N. Pitts Jr., Rates of oxidation of SO₂ in the troposphere, in *Atmospheric Chemistry: Fundamentals and Experimental Techniques*, pp. 646–647, John Wiley, New York, 1986.
- Foltescu, V. L., and E. Selin, Comparison of two dichotomous impactors with different cut-points in field studies of LDT aerosol, in *Fine Particles in Atmospheric Aerosols*, pap. 1, Chalmers Univ. of Technol. and Univ. of Gothenburg, Sweden, 1993.
- Foltescu, V. L., J. Isakson, E. Selin, and M. Stikans, Measured fluxes of sulfur, chlorine and some anthropogenic metals to the Swedish west coast, Atmos. Environ., 28(16), 2639-2649, 1994.
- Foltescu, V. L., E. Selin Lindgren, J. Isakson, M. Oblad, R. Tiede, J. Sommar, J. M. Pacyna, and K. Toerseth, Airborne concentrations and deposition fluxes of major and trace species at marine stations in southern Scandinavia, *Atmos. Environ.*, 30(22), 3857–3872, 1996.
- Gaudichet, A., F. E. Echalar, B. Chatenet, J. P. Quisefit, G. Malingre, H. Cachier, P. Buat-Menard, P. Artaxo, and W. Maenhaut, Trace elements in tropical African savanna biomass burning aerosols, J. Atmos. Chem., 22, 19–39, 1995.
- Hadnagy, W., R. Stiller-Winkler, E. Kainka, U. Ranft, and H. Idel, Influence of urban particulate air pollution (PM10; PM2.5) on the immune system of children, J. Aerosol Sci., 29, suppl. 1, S997–S998, 1998.
- Harrison, R. M., and W. T. Sturges, The measurement and Interpretation of Br/Pb ratios in airborne particles, *Atmos. Environ.*, 17(2), 311–328, 1983.
- Helsel, D. R., Less than obvious: Statistical treatment of data below detection limit, *Environ. Sci. Technol.*, 24(12), 1766–1774, 1990.

- Hinds, W. C., Atmospheric aerosols, in Aerosol Technology Properties, Behavior, and Measurement of Airborne Particles, 280 pp., John Wiley, New York, 1982.
- Hornberg, C., L. Maciuleviciute, N. H. Seemayer, and E. Kainka, Induction of sister chromatid exchanges (SCE) in human tracheal epithelial cells by the fractions PM-10 and PM-2.5 of airborne particulate, *Toxicol. Lett.*, 96-97, 215–220, 1998.
- Kent, G. S., C. R. Trepte, K. M. Skeens, and D. M. Winker, LITE and SAGE II measurements of aerosol in the Southern Hemisphere upper troposphere, J. Geophys. Res., 103(D15), 19,111–19,127, 1998.
- Langmann, B., M. Herzog, and H. Graf, Radiative forcing of climate by sulfate aerosols as determined by a regional circulation chemistry transport model, *Atmos. Environ.*, 32(16), 2757–2768, 1998.
- Liu, X., P. K. Hopke, D. Cohen, and G. Bailey, Sources of fine particle lead, bromine, and elemental carbon in south-eastern Australia, Sci. Total Environ., 175, 65–79, 1995.
- Lobert, J. M., W. C. Keene, J. A. Logan, and R. Yevich, Global chlorine emissions from biomass burning: Reactive chlorine emissions inventory, J. Geophys. Res., 104(D7), 8373-8389, 1999.
- Maenhaut, W., and K. Akilimali, Study of the atmospheric aerosol composition in equatorial Africa using PIXE as analytical technique, *Nucl. Instrum. Methods Phys. Res.*, Sect B, 22, 254–258, 1987.
- Moloi, K., M. Stikans, and S. Chimidza, Elemental concentrations in fine and coarse airborne particles of urban aerosols in Botswana, Africa, J. Aerosol Sci., 29, suppl. 1, S239–S240, 1998.
- Sarangapani, R., and A. S. Wexler, The role of dispersion on particle deposition in human airways, J. Aerosol Sci., 29, suppl. 1, S311–S312, 1998.
- Seinfeld, J. H., Aqueous-phase atmospheric chemistry, in Atmospheric Chemistry and Physics of Air Pollution, pp. 196–198, John Wiley, New York, 1986.
- Seinfeld, J. H., and S. N. Pandis, Halogen-containing compounds, in Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, pp. 86–91, John Wiley, New York, 1998.
- Selin, E., M. Oblad, P. Standzenieks, and J. Boman, Polarization effects in a Si(Li) detector, X Ray Spectrom., 20, 325–330, 1991.
- Selin Lindgren, E., K. Moloi, M. Stikans, and S. Chimidza, Levels and sources of particle air pollution in Botswana studied by EDXRF technique, in *Proceedings of the European Conference on Energy Dispersive X-Ray Spectrometry 1998*, pp. 269–273, Bononia Univ. Press, Bologna, Italy, 1999.
- Sokolik, I. N., and O. B. Toon, Direct radiative forcing by anthropogenic airborne mineral aerosols, *Nature*, 381, 681-683, 1996.
- Standzenieks, P., and E. Selin, Background reduction of x-ray fluorescence spectra in a secondary target energy dispersive spectrometer, *Nucl. Instrum. Methods*, 165, 63–65, 1979.
- StatSoft, Factor analysis, in *Statistica for Windows*, vol. 3, *Statistics*, pp. 3185–3222, Tulsa, Okla., 1994.
- Tillman, D. A., Trace metals in coal and lignite and petroleum fuels, in *Trace Metals in Combustion Systems*, pp. 92–109, Academic, San Diego, Calif., 1994.
- Van Espen, P., K. Janssens, and J. Nobels, AXIL-PC: Software for the analysis of complex x-ray spectra, *Chemom. Intell. Lab. Syst.*, 1, 109-114, 1986.

S. Chimidza and K. Moloi, Environmental Physics Department, Chalmers University of Technology–University of Gothenburg, S-41296 Gothenburg, Sweden. (chimidzs@fy.chalmers.se; mfymoloi@fy.chalmers.se)

(Received October 13, 1999; revised February 4, 2000; accepted March 10, 2000.)

17,818