X-RAY SPECTROMETRY
X-Ray Spectrom. 2005; **34**: 118–123
Published online 13 September 2004 in Wiley InterScience (www.interscience.wiley.com). DOI: 10.1002/xrs.771

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Trace element categorization of pollution sources in the equator town of Nanyuki, Kenya

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Received 10 October 2002; Accepted 15 December 2003

An air pollution campaign was carried out in the town of Nanyuki at four different sites during July and August 1999. Nanyuki is situated on the equator on the northwestern slope of Mount Kenya at about 1930 m above sea level. The intention of the project was to characterize aerosol elemental compositions in two size fractions, associated with specific natural and anthropogenic activities. A dichotomous impactor was used for sampling and an energy-dispersive x-ray fluorescence spectrometer was used for the analysis. Fourteen elements (Si, S, K, Ca, Ti, Mn, Fe, Cu, Zn, Ga, Br, Rb, Sr and Pb) were analysed in all the samples. The concentration of Pb was highest at a site in the vicinity of open-air vehicle garages. The four sites recorded high concentrations of fine S, Cl and K. Fine Zn and Br were also measured at all the sites. In the coarse size range, the concentrations of soil-derived elements (Si, K, Ca and Fe) were dominant. The high concentration of coarse Cl was considered to be due to the contribution of sea salt and that of S to be a contribution of gas to particle conversion of SO_2. The two elements S and Cl signified the influence of long-distance transported aerosols. The comparatively high concentrations of fine Pb and Br signified the high rate of vehicle repairs, which is a major activity close to one of the sites. Generally, soil dust-derived particles and those from biomass burning dominated the town aerosols. Copyright © 2004 John Wiley & Sons, Ltd.

INTRODUCTION

Air pollution is of great concern with respect to human health. It is also of major importance in climate studies and consequently a global concern. Epidemiological studies have found correlations of airborne fine particles (of aerodynamic diameter <2.5 μm, PM2.5) with human morbidity and mortality.[1] These particles affect climate by scattering or absorbing solar radiation, hence interfering with the Earth's radiation budget and as a result climate perturbation.[2,3] Their effect on light scattering interferes with visibility, thus influencing the public perception of air pollution. They are also transported over long distances and are fundamental to studies of aerosol effects on global climate.[4] Ecological impact, health effects, biogeochemical cycles and the characteristics of aerosols are determined by both chemical and physical properties of aerosols. The chemical composition of size-segregated aerosols gives valuable information on the sources and source processes, hence providing clues on how to reduce the atmospheric levels of particulate species.[5] There remain wide gaps in our knowledge of aerosols, especially those in developing countries, creating large uncertainties in estimating the effects of aerosols on global climate. This problem could easily be reduced by the availability of affordable and sustainable air pollution measurement instrumentation in the developing countries.

Mount Kenya tropospheric aerosols are important for improving our knowledge on aerosols measured in the tropics and also inter-hemispherical and transboundary aerosol influences. The characteristics of aerosols in the vicinity of Mount Kenya need to be studied to facilitate the ability to distinguish between long-range transported aerosols and those from local sources. Anthropogenic-derived S and Fe aerosols from both southernmost and central southern Africa may be observed on Mount Kenya after transport of >6000 km. Locally derived aerosols are also frequently transported up the slopes of Mount Kenya, in daytime, in convective and upslope winds.[6] To achieve an understanding of the characteristics of the locally derived aerosols, measurements have to be carried out in the towns around the mountain. Nanyuki is representative of such towns. Air quality in small cities must still be recognized as a powerful aid to understanding pollution issues in large urban areas.[7]

The study reported in this paper relates to a measurement campaign conducted in Nanyuki in July and August 1999. A dichotomous impactor was employed for sampling during the campaign. It sampled two segregated sizes of suspended particles, fine particles having an aerodynamic diameter of <2.5 μm and coarse particles in the range 2.5–10 μm. The samples were obtained from four sites in Nanyuki (Fig. 1). Energy-dispersive x-ray fluorescence spectrometry (EDXRF) was used to analyse both the fine and coarse samples. The aim of this study was to use the concentrations of the analyte

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Contract/grant sponsor: International Science Programme, Uppsala University, Sweden.
Cooperating Institution: Chalmers & Goteborg University Sweden, University of Nairobi, Kenya.

elements to evaluate and assess the most probable sources of the elements with regard to the activities in the vicinity of the sampling site. In the absence of clear local sources, long-distance transport was considered.

EXPERIMENTAL

The aerosol measurement campaign took place in Nanyuki on the northwestern slopes of Mount Kenya. Nanyuki is situated on the equator at 37° east (Fig. 1). It is a busy agricultural and tourist centre and a gateway to Mount Kenya forest and the northeastern region of Kenya. Its eastern, northern and northwestern hinterlands are the savannah plains of Laikipia, which are heavily grazed and cultivated. The main agricultural activities in the hinterland are cattle and wildlife ranching, horticulture, wheat growing, forestry and intensive small-scale farming. The sites selected for sampling are denoted A, B, C and D in Fig. 1. A was near a gasoline station, B was within a small-scale business area, C was 1 km away from the major road joining the southern and northeastern regions of Kenya, situated in a built-up area where building activities are common, and D was at the southeastern outskirts of the town in a low-density residential area where small-scale farming takes place. The sampler was placed 5 m above ground at site A, 6 m at B, 25 m at C and 1.5 m at D. The town's elevation is such that it is inclined from site A towards D, making sites A and C higher into the atmosphere than B and C. The measurement period was generally dry and surface winds were predominantly southeasterly. The wind speed varied from 2 to 5 m s^{-1}, atmospheric pressure from 820 to 822 hPa, temperature from 10 to 25 °C and humidity from 44 to 89%. This meteorological information was obtained from the Department of Meteorology, Ministry of Transport and Communication, Kenya.

The sampling instrument was a dichotomous air sampler (Sierra Instruments, USA)[8] that segregates the airborne particles into two size ranges, fine and coarse, as described above. The sampler had a 10 μm cutoff size-selective inlet. The flow in the impactor was 1 m^3 h^{-1}, provided by a vacuum pump. Samples were collected on Teflon filters of 37 mm diameter and pore size 2 μm. Particles were deposited on an area 29 mm in diameter. The sampler used 10% of the flow to deposit by impaction the coarse particles and 90% to deposit the fine particles on their respective Teflon filters. Teflon filters were tested and found to retain aerosol particles with high efficiency.[9] Sampling took place in July and August 1999. A total of 50 samples of each size range were obtained from the four sites. The sampling time was 24 h for each sample. Since only one impactor was available, sampling was conducted on different consecutive days for each site.

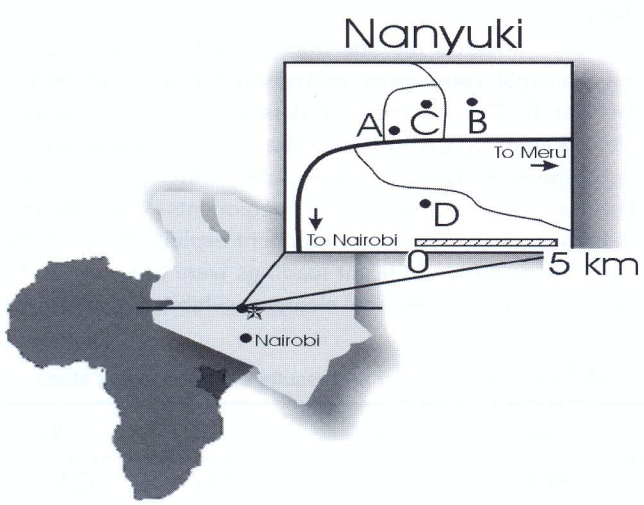

Figure 1. Location of the sampling sites A, B, C and D in Nanyuki.

EDXRF was used to analyse the air samples. This method provides an advantageous compromise between truly multi-element characteristics, satisfactory speed, economy and ease of operation. It is therefore often used for analyses of environmental samples.[10] In comparison with other methods, it does not require any air sample preparation and does not destroy the sample. The EDXRF spectrometer used is at Chalmers University of Technology, Göteborg, Sweden, and was described by Boman.[11] It is a laboratory-built spectrometer with a W-anode x-ray tube and an Mo secondary target. A manually driven sample holder is provided, which makes it easier to load the sample and position the filter surface containing the aerosols at 45° to the exiting x-ray beam. The primary beam illuminates a secondary Mo target, which then emits characteristic Mo photons that excite the elements in the sample. The geometric arrangements between the primary x-ray beam source, the secondary target, the sample and the detector are made close to facilitate high x-ray beam intensity and reduced background.[12] A Si(Li) detector with an active area of 80 mm^2 detected the fluoresced characteristic lines of the elements from the sample. The detector full width at half-maximum (FWHM) for Mn Kα at 5.9 keV was 175 eV. The detected signals were processed by a Kevex 4530P pulse processor set at 6 μs shaping time and a Nuclear Data multi-channel analyser. Each spectrum was acquired for 500 s at a tube voltage of 55 kV and a tube current of 25 mA. The spectra were evaluated using the AXIL program. For the quantification of the elemental concentrations in the samples, a calibration file was created using single-element thin sample standards whose matrix approximated those of the air samples. The program used to quantify the concentrations was QXAS. Bernasconi and Tajani[13] described both the AXIL and QXAS programs. The latter program gave the concentrations in μg cm^{-2}, which were converted to atmospheric concentrations in ng m^{-3} taking into account the diameter of the particle deposit area on the filter and the sampling volume.

Table 1 gives the detection limits (DL) of 15 elements calculated from the spectra of thin standards that were analysed for 300 s at a tube voltage of 55 kV and a current of 25 mA. The standard spectra were evaluated for background area (N_B) and element net peak area (N_P), which were then applied to the IUPAC minimum detection limit equation, $DL = 3C\sqrt{N_B}/N_P$, where C is the certified concentration of the element of interest. Table 2 shows the certified values of NIST SRM 1577a, a multi-element standard, and the average values obtained in analysing the same standard

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Table 1. Detection limit (DL) for various elements using a live time of 300 s, a tube voltage of 55 kV, a tube current of 25 mA and an aerosol collection time of 24 h

Element	DL (ng m^{-3})
Si	240
S	100
Cl	20
K	10
Ca	4
Ti	4
Mn	2
Fe	1
Cu	1
Zn	1
Ga	1
Br	2
Rb	2
Sr	3
Pb	3

12 times for 100 s. Comparison of the values shows a spread of approximately 15% from the certified values.

RESULTS AND DISCUSSION

Table 3 gives the average concentrations of the elements measured in the fine fraction size range. The four sites had relatively high concentrations of Cl, K, Ca and Fe in comparison with previous measurements at the same town.[14] Fine Si was below the DL at all sites. Fine Zn and Br were comparatively low at site D whereas Ti, Mn, Cu, Rb and Pb were below the DLs. Significant differences in the mean concentrations of S, Cl, K, Ca and Ti were recorded between the sites. Fine Br and Pb exhibited similar concentrations at sites A and B. The concentrations of fine Cu and Rb were above the DL only at site B. Normally the concentration of Fe is higher in fine soil dust aerosols than that of Ca, but this was not so evident at site C. The small concentration difference suggested more dust from building construction activities. The comparable concentrations of fine Br and Pb at sites A, B and C implied traffic emissions mainly from the tetraethyllead-B (TEL-B) gasoline still in use in Kenya. The observed ratio of fine Br to Pb was higher than the expected TEL-B ratio of 0.77 in fresh car exhaust,[15,16] implying more sources of the two elements. The highest fine and coarse Pb concentrations were found at site B. This site was characterized by many open-air garages where a skilled labour force is working on vehicle repairs, welding, battery repairs and electrical wiring and repairs. The high concentrations of S, Cl and K in the fine range of particles suggested long-distance transported aerosols, which could originate from biomass burning enriched with sulfates. The enriching sulfate would probably be from both biomass burning and secondary S from gas to particle conversion of SO_2, strengthening the notion of long-range transport. Formation of sulfate takes place in the atmosphere during long-distance transport. Fine Zn and Pb were highest at site B, signifying multiple sources, which could be vehicle emissions, welding and burning of oil-contaminated rubbish. The soil dust elements of Ca, Ti, Mn and Fe would also have been contributed from the dust burnt together with waste in the town.

Table 3. Average atmospheric concentrations in ng m^{-3} of measured elements in the fine size range of sampled aerosols[a]

	A ($N = 10$)	B ($N = 20$)	C ($N = 10$)	D ($N = 10$)
S	610 ± 120	390 ± 30	670 ± 50	270 ± 30
Cl	970 ± 300	390 ± 50	230 ± 5	210 ± 20
K	800 ± 220	540 ± 40	400 ± 22	100 ± 20
Ca	70 ± 10	20 ± 3	120 ± 10	40 ± 20
Ti	7 ± 1	6 ± 1	14 ± 1	<DL[b]
Cr	<DL	1 ± 0.1	<DL	<DL
Mn	3 ± 0.4	5 ± 1	5 ± 0.1	<DL
Fe	70 ± 10	60 ± 10	140 ± 9	80 ± 50
Co	<DL	15 ± 10	<DL	<DL
Cu	<DL	1 ± 0.3	<DL	<DL
Zn	5 ± 1	8 ± 2	5 ± 0.3	2 ± 0.3
Br	13 ± 2	12 ± 1	7 ± 0.2	2 ± 1
Rb	<DL	2 ± 1	<DL	<DL
Pb	10 ± 2	13 ± 2	8 ± 0.3	<DL

[a] N = number of samples; A is the site near traffic, B the site within small businesses, C the site 1 km away from the major road joining the southern and northern regions of Kenya and D the site at the southeastern outskirts of the town in a low-density residential area.

[b] <DL = below detection limit

Figure 2 shows the fine fraction elemental loadings of the principal component analysis (PCA) receptor model for site B. This method of data evaluation for source identification has the advantage that no *a priori* knowledge of the number and type of the particulate sources is required.[17] The model gave four significant components explaining 88% of the variances. The first component explained 31% of the variances and its significant loadings were those of Ca, Ti, Mn, Fe and Cu. These same elements exhibited a significant

Table 2. Comparison of certified elemental concentrations (μg g^{-1}) in SRM 1577a bovine liver and results obtained in this study

	S	K	Mn	Fe	Cu	Zn	Rb
Certified value	7800 ± 100	9960 ± 70	9.8 ± 0.8	194 ± 20	158 ± 7	123 ± 8	12.5 ± 0.1
This study[a]	7200 ± 950	9750 ± 900	12.2 ± 3.5	241 ± 18	170 ± 10.4	145 ± 7	15 ± 2

[a] The measured values are given as the mean concentrations of 12 measurements ±1 standard deviation

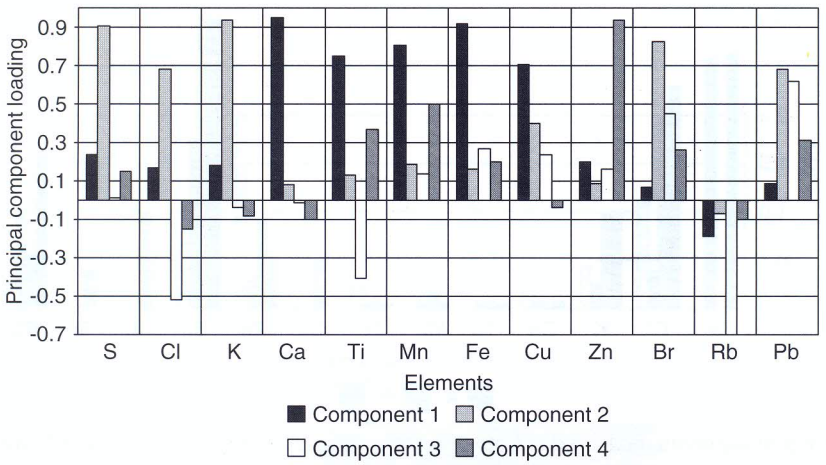

Figure 2. Principal component loadings of the fine fraction size range measured at site B, the site within the small businesses. Fine Si was below the detection limit.

correlation at $p < 0.05$. Ca and Fe had the highest significant correlation of 0.86 and highest loading in this factor. The elements in this factor are those from the soil dust, making the factor represent a source contribution of windblown and resuspended dust to the fine fraction. The second component explained 28% of the variances. Its loadings of significance were those of S, Cl, K, Br and Pb. The correlation of Br and Pb was >0.9 whereas S and Cl had a weak correlation of 0.55. This component was assigned to biomass burning and vehicle emissions, which were enriched with sulfates. There are no industries in Nanyuki burning fossil fuel that could justify the high S concentration. Consequently, some of the S may have been transported over a long distance and contributed by oxidation of SO_2 to sulfates. The third component explained 17% of the variances and was loaded by Rb and Pb, depicting gasoline and wood burning. Pb was correlated with S, K and Br. The fourth component had Zn as the significant loader. The same element was significantly correlated at $p < 0.05$ with Mn, a soil dust element. This correlation implied a soil dust relation making the component suggest a source of particles from burning of oil-contaminated waste, which was soiled. The component explained 12% of the variances.

Table 4 gives the concentrations of the measured elements in the coarse fraction size range. The soil-derived elements Si, K, Ca, Ti, Mn and Fe had variable concentrations at the different sites, signifying localized sources. Coarse S was not detected at sites B and D. The detected coarse S at sites A and C may have been from wood and oil-contaminated waste burning or resuspension of sulfate-containing particles. Site C recorded the highest concentrations of crustal elements (Si, K, Ca, Ti, Mn and Fe), suggesting soil-derived dust near the site. The sampler at site C was at 25 m above ground, which would mean that the prevailing winds sustained coarse dust particles at greater heights than the lower ones. However, the site was in an area where there were building works on storeyed houses and the building materials could be the source of the high concentrations. The coarse Pb concentration was highest at site B with those at A and C being a factor of three lower. This Pb implied that there was mixing of leaded gasoline with soil dust, hence becoming part of it, and increased vehicle battery repairs in the area. The presence of Zn and Pb at sites A, B and C suggested that the elements could have originated from resuspended soil dust, which contained lubricating oils. Zn is a tracer of lubricating oil.[18] The coarse Cl concentration was comparable at sites A and C, and also at sites B and D, with the former sites having concentrations higher by a factor of two than the latter sites. The most probable source of this Cl could be sea salt that may have been brought from the Indian Ocean by the southeasterly winds. Gatebe[19] reported that southeasterly winds were predominant during the period from May to September.

Figure 3 is a graphical representation of fine to coarse ratios, which give an insight into the weight that anthropogenic activities have on suspended particles.[18] The ratio for S was >1 at sites A and C, and that for Br was also >1 at sites A, B and C. The ratio for Cl was >1 at sites A,

Table 4. Average atmospheric concentrations in ng m^{-3} of measured elements in the coarse size range of sampled aerosols[a]

	A ($N = 10$)	B ($N = 20$)	C ($N = 10$)	D ($N = 10$)
Si	3100 ± 500	2500 ± 460	6000 ± 450	900 ± 130
S	230 ± 30	<DL[b]	260 ± 40	<DL
Cl	420 ± 60	200 ± 20	580 ± 70	190 ± 30
K	830 ± 140	550 ± 80	1520 ± 100	230 ± 40
Ca	810 ± 170	460 ± 70	1700 ± 170	110 ± 8
Ti	120 ± 20	90 ± 20	240 ± 20	40 ± 7
Mn	50 ± 9	30 ± 6	100 ± 7	<DL
Fe	1200 ± 220	820 ± 150	2400 ± 160	360 ± 60
Cu	1 ± 0.3	2 ± 1	2 ± 0.1	14 ± 2
Zn	9 ± 2	9 ± 1	16 ± 1	1 ± 0.2
Ga	1 ± 0.1	1 ± 0.1	2 ± 0.1	<DL
Br	3 ± 0.5	4 ± 0.4	3 ± 0.1	<DL
Rb	3 ± 0.4	2 ± 0.3	5 ± 0.3	<DL
Sr	8 ± 1	5 ± 1	15 ± 1	<DL
Pb	6 ± 1	24 ± 8	8 ± 0.3	<DL

[a,b] See Table 3.

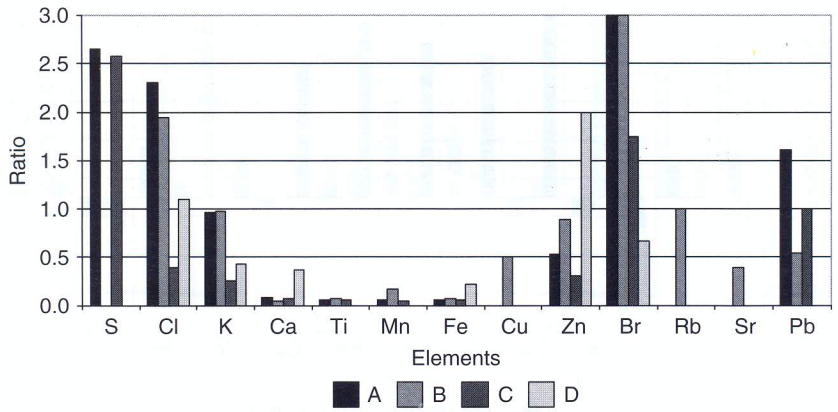

Figure 3. Fine to coarse ratio of elements measured in both fine and coarse size ranges. A, B, C and D denote the sampling sites which are described in the text and locations shown in Fig. 1.

B and D whereas that of Pb was >1 at site A and Zn at site D. Ratios >1 indicated that the elements were mainly in the fine fraction. Fine fraction particles have a long residence time in the atmosphere and may be transported for long distances. The high ratios for some of the elements may have been due to their being enriched by long-distance transported aerosols. The transport of the aerosols was by the predominantly southeasterly winds that prevailed in the area. Pb and Zn at site B were predominantly in the coarse fraction. This strengthened the notion that they were a component of the resuspended soil dust and other repair activities in the vicinity of site B. Most of the elements had fractional ratios, placing them in the coarse fraction range of suspended particles. This implied that the Nanyuki aerosols were dominated by coarse particles which were mainly soil dust derived.

International standards of air quality for Mn, Zn and Pb are 150 ng m^{-3} of Mn and 500 ng m^{-3} of Pb according to WHO,[20] 100 μg m^{-3} of Zn and 3 μg m^{-3} of Pb according to EEA[21] and 1.5 μg m^{-3} of Pb according to USEPA[22] guidelines. The measured concentrations in Nanyuki were far below the stipulated guideline concentrations. The comparison with international and other national guidelines was necessary since Kenya has no air quality guidelines. The measured concentrations were also compared with concentrations obtained by others in different parts of Africa[23–25] (Table 5). Fine Pb and Br concentrations were higher in Gaborone in Botswana and Dar es Salaam in Tanzania than those measured in Nanyuki. Dar es Salaam and Gaborone are major cities in their respective countries and one would expects higher concentrations of vehicles in such cities in Africa. Vehicle exhaust is a major source of Br and Pb. Concentrations of fine S, Cl and K were lower in both urban and rural Botswana than that measured in this study except S in Serowe, which was higher. This implied that biomass burning and marine aerosols had a higher influence in Nanyuki than in the towns in Botswana. Serowe is near a major coal-fired power plant,[23] which could be

Table 5. Summary of elemental concentrations in aerosol particles (in ng m^{-3}) from different measurements in Africa[a]

	Chimidza and Moloi[23]						Chimidza[24] Gaborone[b]		Kololeni[25] Dar es Salaam[c]	
	Serowe[b]		Selibe-Phikwe[b]		Francis Town[b]					
	Fine (mean)	Coarse (mean)	Fine (mean)	Coarse (mean)	Fine (mean)	Coarse (mean)	Fine (mean)	Coarse (mean)	Fine (max.)	Coarse (max.)
Si		4900		7800		3900		4400		
S	960		320		320		120	130	220	310
Cl	100	210	80	310	77	230	100	110	130	100
K	450	290	250	840	320	350	650	590	370	540
Ca	160	2400	77	830	55	690	160	760	520	3800
Ti	15	160	22	240	8	110	41	190	60	60
Mn	6	47	6	55	3	28	14	53	300	260
Fe	210	2100	320	3100	110	1300	600	2400	830	880
Cu	3	8	3	22	1	5	7	10	300	310
Zn	6	10	4	13	4	7	28	21	820	410
Br	8	1	12	5	9	2	120	15	100	800
Pb	9.5	3.6	22	15	11	5.6	230	38	790	970

[a] Fine = particles with aerodynamic diameter <2.5 μm, coarse = particle size range 2.5–10 μm.
[b] Samples were collected for 12 h.
[c] Samples were collected for 24 h.

responsible for the higher concentration of S. The same three elemental concentrations were lower in Dar es Salaam than at Nanyuki. Biomass burning was a dominant source of Nanyuki fine aerosols and it is a major source of K and Cl. The concentration of coarse Cl was also higher in Nanyuki than in Dar es Salaam and Botswana towns. Marine aerosols are a major source of coarse Cl. Dar es Salaam is on the Indian Ocean coast and one would expect higher concentrations of coarse Cl in Dar es Salaam than in Nanyuki. Probably the wind direction in Dar es Salaam may have reduced the marine aerosol influence at the sampling site. However, the difference is further evidence of long-range transported sea salt particles during the prevailing weather conditions. Comparison of our measured concentrations of fine S, Fe, Br, Pb, Zn and Cu with those measured in Beijing[7] in China, Kyoto[7] in Japan, Mexico City[7] in Mexico, Milan[26] in Italy, Birmingham[27] in the UK and Los Angeles[27] in the USA shows that Nanyuki concentrations are far lower, implying less air pollution.

CONCLUSIONS

These measurements showed that coarse particle mass concentrations dominated in the aerosols of Nanyuki. Indian Ocean marine aerosols were present in the measured aerosols as implied by the high concentration of coarse Cl, whose main source is sea salt. Biomass burning was a major source of fine suspended particles whereas the activities in small businesses contributed significant mass concentrations of fine Br and Pb by way of traffic emissions from vehicles and batteries under repair. The fine Zn contribution marked the existence of burning of oil within the vicinity of the small businesses.

The fine S may have been due to long-distance transport of SO_2 and its conversion to sulfates. It was difficult to explain how the long-distance transported Cl and S could have reached the sampling sites. However, the dominating southeasterly winds were seen as the means of transport. Consequently, for sea salt and sulfates to reach the sampling sites there had to be a downward transport from the middle to the lower troposphere. Gatebe *et al.*[6] discuss downslope winds on the slopes of Mount Kenya at night and that could be the mechanism of transport of Cl and S from the middle to lower troposphere.

The concentrations obtained during this campaign were higher than those reported previously.[14] Due to biomass burning and the Indian Ocean influence, there were higher concentrations of fine K, Cl and S in Nanyuki than in other towns in Africa. The concentrations obtained were far lower than those measured in some cities in Asia, Europe and the USA implying that Africa is not yet as highly air polluted as the other continents. More measurements at the higher altitude sites on Mount Kenya are necessary to ascertain the trends of regional and interhemispherical aerosol influences on the mountain, especially those of S and Cl.

Acknowledgements

We acknowledge financial support from International Science Programme, Chalmers University of Technology and Göteborg University, Sweden, and University of Nairobi, Kenya. Our thanks are extended to S. K. Bartilol, Institute of Nuclear Science, University of Nairobi, for assisting with data processing.

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