

Atmospheric Levels And Elemental Composition of Fine And Coarse Aerosols During Wet And Dry Season Campaigns At Two Sites In Tanzania

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Abstract. Three aerosol sampling campaigns were conducted at two sites in Tanzania, first in the 2005 wet season (May-June), then in the 2005 dry season (July-September), and finally in the 2006 wet season (March-May). The sites were at Dar es Salaam (a kerbside) and at Morogoro (a rural site; on the main campus of the university), about 200 km to the west of Dar es Salaam. Among the aerosol samplers was a Gent PM10 stacked filter unit sampler with sequential Nuclepore polycarbonate filters, providing coarse (2-10 μm diameter) and fine (<2 μm) size fractions. Depending upon the season and the location, either 24-hour collections or separate daytime and nighttime samplings were performed. The Nuclepore filters were analysed for the particulate mass (PM) by weighing, for black carbon (BC) with a light reflectance technique, and for up to 28 elements by PIXE. The median levels of the PM10 PM for the three campaigns were 23, 45, and 13 $\mu\text{g}/\text{m}^3$ at Morogoro and 45, 58, and 40 $\mu\text{g}/\text{m}^3$ at Dar es Salaam. The average percentages of the PM10 mass in the fine size fraction during the three campaigns were 35, 49, and 37% at Morogoro and 31, 27, and 32% at Dar es Salaam. Most elements were predominantly associated with the coarse size fraction; notable exceptions were BC, S, K, and Pb, and at Dar es Salaam also V, suggesting that BC and these elements originated mainly from anthropogenic sources. Some typical anthropogenic elements, i.e., Zn and Pb, exhibited 20-70 times higher median PM10 levels at Dar es Salaam than at Morogoro. The high median levels for these elements at Dar es Salaam (e.g., 270 ng/m^3 for Zn and 113 ng/m^3 for Pb during the dry season campaign) are likely mainly due to local industrial sources.

Keywords: atmospheric aerosols, PM10, chemical composition, aerosol sources, Tanzania.

INTRODUCTION

Very little information is currently available on atmospheric aerosol levels and composition for Tanzania. The few published studies so far dealt with concentrations of the suspended particulate matter (SPM) and of particulate elements in Dar es Salaam [1-4]. In order to obtain an idea of the current levels of the fine (<2 or <2.5 μm), coarse, and PM10 particulate matter and its composition, which could serve as a reference for further studies in this developing country, aerosol collections were conducted at two sites in Tanzania during three sampling campaigns (two campaigns in 2005 and one in 2006). PM2.5 and PM10 filter samplers and a "Gent" PM10 stacked filter unit (SFU) sampler were deployed and the samples were analysed by several techniques to obtain a comprehensive aerosol characterisation. Here, we

present and discuss the results from the elemental analyses by PIXE of the SFU samples and some other data for these samples. Emphasis is given to the examination of the seasonal variability and the day/night differences in the atmospheric concentrations of the elements and the particulate mass (PM) and to assessing the sources of certain elements or aerosol components.

EXPERIMENTAL

The aerosol collections in Tanzania were done at a rural site in Morogoro and at a kerbside site in Dar es Salaam. Three sampling campaigns took place, first in the 2005 wet season (May-June), which was actually rather dry, then in the 2005 dry season (July-September), and finally in the 2006 wet season (March-May). During each campaign, the aerosol

samplers were first deployed in Morogoro and then transferred to Dar es Salaam for deployment there. Morogoro (270,000 inhabitants) is situated at about 200 km in westerly direction of Dar es Salaam. The sampling site in Morogoro was on the main campus of Sokoine University of Agriculture (6°49'S, 37°39'E, altitude 526 m a.s.l.). The samplers were mounted on a roof approximately 6 m above ground level. This site is purely a residential area and far from major road systems. The main local sources are expected to be wind-blown soil dust and biomass burning, mainly for domestic heating and cooking. In Dar es Salaam (ca. 3 million inhabitants), the sampling was conducted on the second-floor balcony (about 10 m above the ground level) of the Young Women's Christian Association of Tanzania (YWCA) building (6°48'S, 39°17'E, altitude 4 m a.s.l.), which is located along one of the major paved roads (Azikiwe street) in the city. This site can be classified as a kerbside according to Van Dingenen et al. [5]. Traffic, sea spray and ships from the harbour, and heating for domestic, restaurant, and commercial activities are the main local sources. There are also a battery industry and several metal processing industries within 10 km from this sampling site.

Among the aerosol samplers was a "Gent" PM10 SFU sampler [6] with coarse (Apiezon-coated) and fine Nuclepore polycarbonate filters of 47 mm diameter (pore sizes 8 and 0.4 μm , respectively), placed in series. This sampler was operated at a flow rate of about 17 L/min, so that the coarse filter collected the 2-10 μm aerodynamic diameter (AD) size fraction and the fine filter the particles <2 μm AD.

Depending upon the season and the location, either 24-hour collections or separate daytime (7:00–19:00) and nighttime (19:00–7:00) samplings were performed. The number of SFU filter sample pairs in the three campaigns was 13, 51, and 29 for the Morogoro site and 16, 63, and 55 for Dar es Salaam, with 24-hour samplings in the 2005 wet season campaigns and in the 2006 wet season campaign at Morogoro and separate daytime and nighttime samplings in the other cases. The Nuclepore filters were analysed for the PM by weighing, for black carbon (BC) with a light reflectance technique, and for up to 28 elements (from Na to Pb) by PIXE. The weighings were done at 20°C and 50% relative humidity and the filters were pre-equilibrated at these conditions for at least 24 hours. Details upon the light reflectance technique used for BC and upon the PIXE analyses can be found in [7] and in the references therein. Although also PIXE data will be reported here for Na and Mg, it should be indicated that these data have a large associated uncertainty because of strong matrix effects (i.e., X-ray attenuation and particle size effects).

RESULTS AND DISCUSSION

Concentrations, Day/night Differences And PM2 To PM10 Ratios

The median concentrations (and interquartile ranges) of the PM10 mass concentration (sum of coarse + fine) for the PM, BC, and up to 23 elements

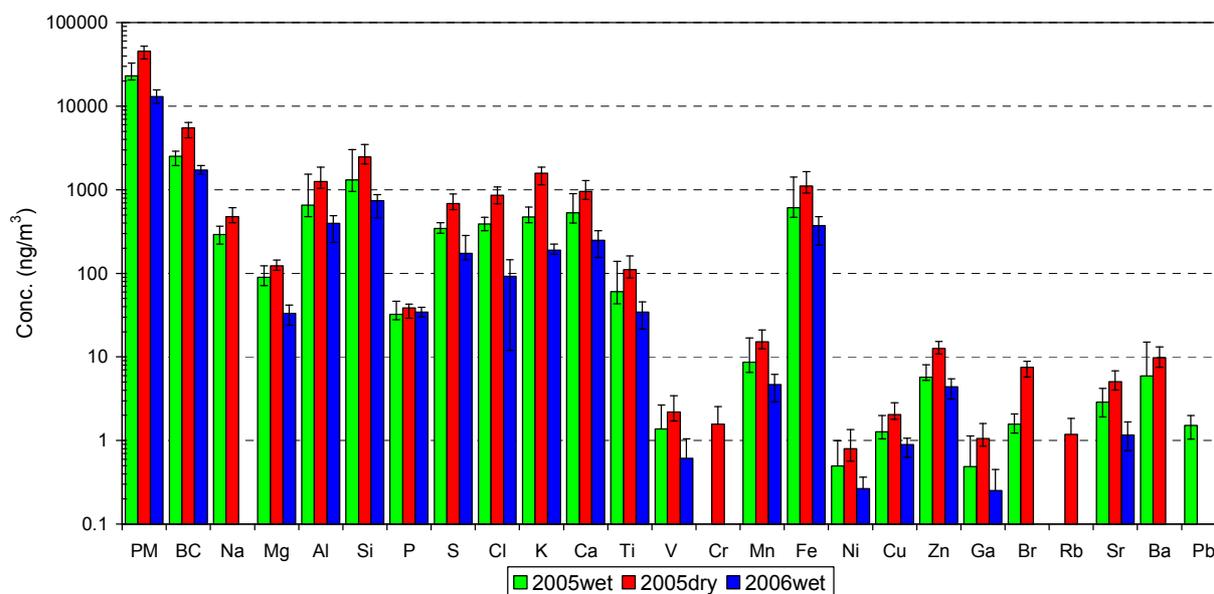


FIGURE 1. Medians (and interquartile ranges, denoted by the bars) of the PM10 mass concentration for the PM, BC, and 23 elements in the three campaigns for the rural site at Morogoro, Tanzania.

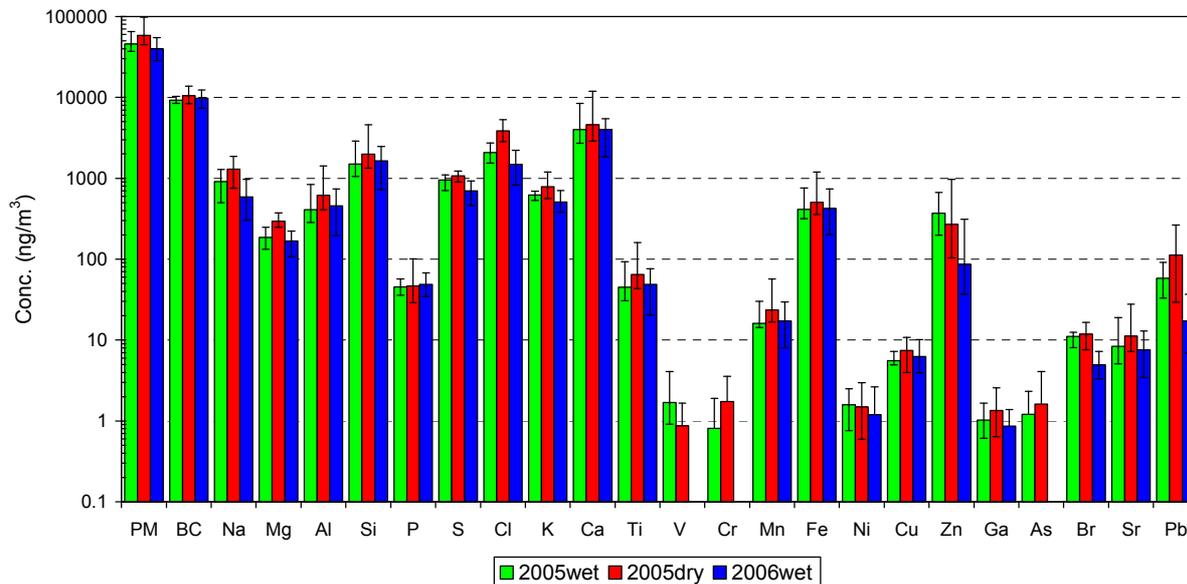


FIGURE 2. Medians (and interquartile ranges, denoted by the bars) of the PM10 mass concentration for the PM, BC, and 22 elements in the three campaigns for the kerbside site at Dar es Salaam, Tanzania.

in the three campaigns are shown in Figure 1 for Morogoro and in Figure 2 for Dar es Salaam.

At each site, the highest levels for the PM, BC, and most elements were observed during the dry season campaign and the lowest levels during the 2006 wet season campaign. Furthermore, and as expected, the levels are higher at the Dar es Salaam kerbside than at the rural Morogoro site. For example, for the PM10 PM the median levels in the three campaigns were 23, 45, and 13 $\mu\text{g}/\text{m}^3$ at Morogoro and 45, 58, and 40 $\mu\text{g}/\text{m}^3$ at Dar es Salaam. The difference between the two sites was particularly pronounced for some typical anthropogenic elements, such as Zn and Pb; these two elements exhibited 20-70 times higher median PM10 levels at Dar es Salaam than at Morogoro, suggesting strong local sources for these elements in Dar es Salaam. The levels of Zn and Pb were also quite variable at this site (note the large interquartile ranges in Figure 2), which suggests that the impact from the local sources varied with change in emission intensity or wind direction.

Another particular feature for the Dar es Salaam site were the very strong day/night differences for the crustal elements (Al, Si, Ca, Ti, Fe). This was particularly obvious in the 2005 dry season campaign. For example, during this campaign, the average ratio of the PM10 level during the day to that during the subsequent night was 3.3 ± 1.0 (N=31) for Al, Si, and Fe. In contrast, the same type of ratio was for the sea-salt elements Na and Cl respectively 0.7 ± 0.4 and 1.1 ± 0.4 , and for the essentially anthropogenic element S 1.3 ± 0.3 . This indicates that the day/night differences

for the crustal elements are not due to differences in boundary layer height between day and night; actually, at sites where there are changes in boundary layer height between night and day, one normally observes a more shallow boundary layer (and thus higher concentrations) during the night.

The average percentages of the PM10 mass in the fine size fraction during the three campaigns were 35, 49, and 37% at Morogoro and 31, 27, and 32% at Dar es Salaam, indicating that most of the PM10 mass was in the coarse size fraction, especially at Dar es Salaam. As expected, the crustal and sea-salt elements were even more associated with the coarse size fraction (for the crustal elements typically for about 90%) than was the case for the PM; also P, Cu, and Zn were mainly in the coarse fraction. In contrast, BC, non-sea-salt (nss) S, K, and Pb, and at Dar es Salaam also V, were mostly associated with the fine size fraction suggesting that BC and these elements originated mainly from anthropogenic high-temperature sources (including gas-to-particle conversion for nss-S). Still other elements, such as Ni, had about equal percentages in the two size fractions.

Main Sources For Certain Elements And Aerosol Components

From the concentrations of the crustal elements, the concentration of the crustal aerosol type (component) was calculated for each of the two sites and each campaign. At both sites, the crustal component

accounted for about one third of the PM₁₀ PM. At Morogoro, this crustal component originated most likely mainly from local and regional soil dust dispersal. At the Dar es Salaam kerbside, however, a large fraction of the crustal component is undoubtedly due to resuspended road dust, particularly during the daytime, when the concentrations of the crustal elements and the traffic intensity were much greater than during the night. During the 2005 dry season campaign, the concentration of the crustal component was, on average, 35 $\mu\text{g}/\text{m}^3$ during the daytime and only 10 $\mu\text{g}/\text{m}^3$ during the night; for comparison, the sea-salt concentration (calculated from Na and Cl) was very similar (on average around 9-10 $\mu\text{g}/\text{m}^3$) during day and night. It is therefore reasonable to assume that the day/night concentration difference of 25 $\mu\text{g}/\text{m}^3$ for the crustal matter component is essentially due to road dust. For the PM₁₀ PM in the 2005 dry season campaign at Dar es Salaam, the difference between the average level during daytime and nighttime amounted to 49 $\mu\text{g}/\text{m}^3$, of which 25 $\mu\text{g}/\text{m}^3$ came from crustal matter. The remaining 24 $\mu\text{g}/\text{m}^3$ is likely also partly related to traffic and may to a large extent consist of carbonaceous matter.

To elucidate the sources of the various elements at the two sites, crustal enrichment factors and pairwise correlation coefficients were calculated and various scatter plots were constructed. At both sites, K exhibited substantial enrichment in the fine size fraction, on average, around 10, which is similar as observed at African sites that were heavily impacted by biomass burning and where the pyrogenic aerosols accounted for a large fraction of the PM [8]. This suggests that biomass burning (in this case for heating and cooking) was also a main contributor to the PM at our two sites and in particular to the organic fraction of the PM. Fine V and fine Ni were highly correlated with each other at Dar es Salaam and their concentration ratio was around 2, which is consistent with residual oil burning as a source for these elements. BC and coarse and PM₁₀ Cu were at Dar es Salaam highly correlated with the crustal elements, suggesting that they were related to traffic sources. For BC, automotive exhaust emissions, in particular from diesel trucks, are undoubtedly important. That also Cu comes from traffic is not unexpected, as brake linings wear is a well-known source for this element [e.g., 9]. Also Zn and Pb are in cities often related to traffic, with tire wear and leaded gasoline as important sources [e.g., 10 and references therein]. However, neither Zn nor Pb was strongly correlated with the crustal elements (or with any other element) at Dar es Salaam; besides, the ratio of non-sea-salt Br to Pb was much lower than in particulate emissions from leaded gasoline. It is therefore thought that Zn and Pb originated mainly from industrial emissions in Dar es Salaam, and that different industries were responsible for the two elements. For Pb this could be the battery

industry and for Zn the several metal processing industries, which are all located within 10 km from this sampling site.

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REFERENCES

1. Y. I. A. Koleleni, *Discovery and Innovation* **15** (2003) 203-212.
2. P. Jonsson, C. Bennet, I. Eliasson and E. S. Lindgren, *Atmos. Environ.* **38** (2004) 4175-4181.
3. C. Bennet, P. Jonsson and E.S Lindgren, *X-Ray Spectrom.* **34** (2005) 1-6.
4. M. M. Jackson, *Environ. Monitoring and Assessment* **104** (2005) 385-407.
5. R. Van Dingenen, F. Raes, J.-P. Putaud, U. Baltensperger, A. Charron, M.-C. Facchini, S. Decesari, S. Fuzzi, R. Gehrig, H.-C. Hansson, R. M. Harrison, C. Hüglin, A. M. Jones, P. Laj, G. Lorbeer, W. Maenhaut, F. Palmgren, X. Querol, S. Rodriguez, J. Schneider, H. ten Brink, P. Tunved, K. Tørseth, B. Wehner, E. Weingartner, A. Wiedensohler and P. Wählin, *Atmos. Environ.* **38** (2004) 2561-2577.
6. W. Maenhaut, F. François and J. Cafmeyer, The Gent stacked filter unit sampler for the collection of atmospheric aerosols in two size fractions: description and instructions for installation and use, in *Applied Research on Air Pollution Using Nuclear-related Analytical Techniques*, IAEA Report NAHRES-19 Vienna (1994), pp. 249-263.
7. W. Maenhaut and J. Cafmeyer, *X-Ray Spectrom.* **27** (1998) 236-246.
8. W. Maenhaut, I. Salma, J. Cafmeyer, H. J. Annegarn and M. O. Andreae, *J. Geophys. Res.* **101** (1996) 23631-23650.
9. B. D. Garg, S. H. Cadle, P. A. Mulawa, P. J. Groblicki, C. Laroo and G. A. Parr, *Environ. Sci. Technol.* **34** (2000) 4463-4469.
10. I. Salma and W. Maenhaut, *Environ. Pollution* **143** (2006) 479-488.