DETERMINATION OF SUSPENDED PARTICULATES MATTER OF MAJOR SIGNIFICANCE TO HUMAN HEALTH USING NUCLEAR TECHNIQUES IN KENYA

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Energy dispersive X-ray fluorescence (EDXRF) analysis of aerosol samples in Nairobi is presented. Results show that elemental concentrations are of the order of 10^{-4} to 10^{-6} µg/m³ for most elements analyzed. The total suspended particulate (TSP) matter was between 30–80 µg/m³ for the entire sampling period between December 1993 to October 1994. Levels of lead (Pb) are below WHO guidelines. However, the obtained bromine (Br) to Pb ratio: 0.3–0.51, shows the origin of Pb to be from vehicular emissions. This ratio was particularly high during the months of April to July 1994 which were also found to be very active in terms of weather parameters.

It is increasingly recognized that submicrometer sized atmospheric aerosols have a much greater effect on the earth's radiation balance and thus on regional and global climate.[1] The fine, anthropogenic particles have received a lot of attention. Such particles scatter the incoming solar radiation (direct effect) and they can act as cloud condensation nuclei (CCN) and thereby change the radiative properties of clouds (indirect effect).[2,3] Other anthropogenic and natural fine particles have similar radiative and climatic effects. Examples of such fine particles are those emitted by various forms of wood, charcoal and agricultural waste,[1] while the anthropogenic (biomass burning) particles are pre-dominantly emitted in equatorial and tropical regions such as Brazil, Africa and South East Asia. PENNER et al.[4] and DICKSON[5] estimated that the combined direct and indirect radiative effects of smoke aerosols are responsible for a global reflection of solar radiation that is comparable to that of the sulphate aerosol. Aerosol particles such as iron, copper, manganese and their constituents play an important role in heterogeneous (multi-phase) atmospheric chemistry (and photochemistry) by acting as surfaces and/or catalysts for the reactions on and with various atmospheric trace gases (e.g., oxidation of SO_2 to sulphate). Other important effects of aerosols include the reduction of visibility (by fine particles), their rate in the ecology (e.g., by contributing to "acid rain"), their effects on the welfare and health of human and animals, and on buildings, structures and materials.[1,6–9]

Pollution in Kenya

The little information available related to air pollution in Kenya indicates an upward trend.[10] High concentrations of heavy metals were found in edible portions in a variety of food crops and in the soil within the vicinity of busy arterials. Pb levels of up to 127 µg/g against the normal range of 0.1 to 1.0 µg/g were found in vegetables and cereals.

In Nairobi, which is the capital city of Kenya, there is no systematic air quality monitoring programme. Nairobi is indicated as one of the cities where continuous air System, but data is available only for the period 1977/78.[10,11] Sulphur dioxide (SO_2) and particulate matter were found to be near or above the recommended guidelines at several sites within the city including suburban and industrial areas. Similar results have been obtained by other workers.[3,12,13] Motor vehicles are also predicted to increase the level of pollutants in Nairobi[14,15] (see Table 1). The predicted increase would mainly be due to more vehicles and their deteriorating conditions. Although the actual levels may be significantly different from the estimates, the depicted trends are critical.

Table 1
Estimates of pollutant emissions by passenger cars
and buses in Nairobi (tons per day)[15]

Year	CO	HC	NO_x	SO_2	PM
1986	77	7	4	0.6	0.5
2000	381	38	20	3.0	2.7

The vehicle population within the city is estimated to be at least two-thirds of the national vehicle population.[16] Furthermore, the traffic volume is increased by the large daily commuter traffic between the city and its environs.

In this paper, we describe the use of a nuclear technique; energy dispersive X-ray fluorescence (EDXRF) in air pollution studies in Nairobi. The results presented are part of a continuing co-ordinated research under the International Atomic Energy Agency (IAEA) on the use of nuclear and nuclear related techniques in environmental pollution monitoring. The results are for the period between December 1993–October 1994.

Experimental

Sampling site: The aerosol measurements, started in December 1993 at the Kenya Meteorological Department (KMD) Headquarters, which is about 1798 m above mean sea level and to the north northwest of the city centre, 5 km away. KMD is located in a suburban area surrounded by residential areas. During the sampling period, the average rainfall for the whole period of sampling was 24 mm. The winds were generally easterlies and blowing at 8 knots (4 m/s). The major sources of air pollution in the close proximity are expected to be residential heating and automotive emissions from a major highway.

The site is the headquarter of Meteorological Services in Kenya and as such is equipped with a full-fledged weather station, and a good infrastructure like electricity, and backup power. The weather observers were utilized in data acquisition since the station operates 24 hours a day. The sampler was installed 8 m from the ground on the communication masts close to the observatory station.

Sampling: Sampling was done using the "Gent" stacked filter unit (SFU) supplied by the IAEA.[17] A total of 400 samples were collected between December 1993 and October 1994. On average two sets of samples were collected per week for analysis with EDXRF. The sampler was run at 1 m^3/hour over a 24-hour collection period.

With each sample, the following information was recorded:

– number of the SFU cassette;
– start time and end time;
– initial and final air volume (as read from SFU meter);
– rotameter flow rate at beginning and end of sampling;
– weather conditions (overcast, sunny etc.).

Filters were weighed in an air conditioned laboratory controlled at 50% relative humidity and 20 °C. A ^{241}Am α-emitting source was used to remove the static build up from the filter. Prior to weighing, all filters were left to equilibrate for at least 24 hours.

The SFU was cleaned regularly with ethanol to remove any particles which may have accumulated. Filter handling was done with care and using plastic tweezers to avoid contamination.

Description of "Gent" SFU: As many of the effects of aerosols depend on their size and chemical composition, it is highly desirable to collect the particles in at least two different size fractions (coarse and fine) for subsequent chemical analysis. This is therefore why an SFU was designed by the University of Gent for a co-ordinated research project supported by IAEA and with almost 20 participating countries.

Like other SFU variants,[18,19] Gent SFU is based on sequential filtration through two nucleopore filters with different pore sizes.[20] The coarse filters collects the particles larger than 2 μm equivalent aerodynamic diameter (EAD) and the fine filter for the

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particles < 2 µm EAD.[21] In order to have a well defined upper cut point for the coarse size fraction, the Gent SFU is equipped with a pre-impaction stage, which has a cut-point (also value) of 10 µm EAD and thus act as an inlet.

The division of the particles into two sizes resembles the human respiratory system, in which the coarse particles are stopped in the nasal and bronchial regions, whereas the fine particles can penetrate into the alveoli and possibly be transported into the body systems. The Gent SFU has been calibrated by many workers, amongst them MAENHOUT et al.[1]

EDXRF set up: The EDXRF technique has previously been described by KINYUA.[22] It consists of a Si(Li) detector of resolution 190 eV for Mn K_α line at 5.9 keV, [109]Cd X-ray excitation source (25 mCi) or X-ray tube (Mo) together with associated electronics for signal processing and shaping and a PC based S-100 multichannel analyzer with the relevant interface and software.

Data analysis: Each sample was irradiated for 1000 seconds using the sources. The analyses of the X-ray spectra was done by AXIL[23] and quantitative analysis of environmental samples (QAES) for spectral deconvolution and quantitative measurements.[24]

Results and discussion

In this work, we present the results obtained by EDXRF analysis for size fractionated aerosol samples previously sent for intercomparison (Table 2) and those collected during a 10 month period at the Kenya Meteorological Department (Table 3 and Figs 2–8). The average elemental content of Ca, Mn, Fe, Cu, Zn, Pb and Br for coarse and fine size filters are shown in Table 3. Variations of TSP values for 0.4 and 8 µm filters are shown in Fig. 1.
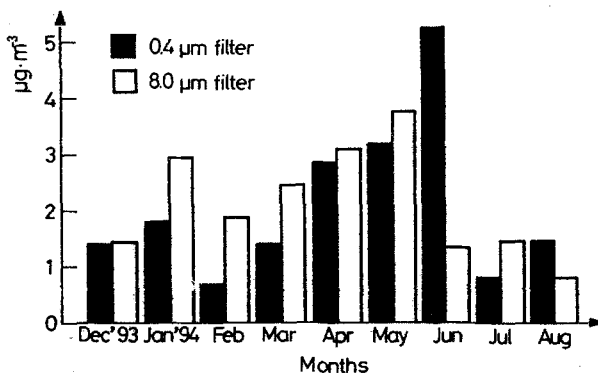

Fig. 1. Variation of TSP

Table 2
Quality control exercise particulate filter standards report

Element	Blank 1	Blank 2	No. 57-Fine Fine	No. 72-Coarse Coarse	Method used (EDXRF)
			(results in µg/filter)		
			(527 µg) (filter wt)	(397 µg) (filter wt)	
K	< 1.63	< 1.27	4.61 ± 1.34	4.78 ± 1.28	^{109}Cd
Ca	20.5 ± 0.16	18.37 ± 0.14	46.57 ± 0.35	24.53 ± 0.18	Tube
Ti	< 0.19	< 0.19	1.83 ± 0.47	1.09 ± 0.32	^{109}Cd
Mn	0.40	0.60 ± 0.17	0.60 ± 0.22	0.64 ± 0.15	^{109}Cd
Fe	1.20 ± 0.18	1.40 ± 0.15	18.87 ± 1.25	10.43 ± 0.70	^{109}Cd
Ni	< 0.20	0.27 ± 0.10	0.46 ± 0.12	0.37 ± 0.08	^{109}Cd
Cu	0.34 ± 0.10	0.45 ± 0.08	< 0.28	0.03 ± 0.07	^{109}Cd
Zn	0.46 ± 0.09	0.36 ± 0.07	0.78 ± 0.10	0.05 ± 0.07	^{109}Cd
Br	< 0.10	< 0.10	< 0.09	< 0.03	^{109}Cd
Rb	< 0.09	0.104 ± 0.036	0.18 ± 0.04	< 0.06	^{109}Cd
Sr	< 0.05	< 0.062	0.18 ± 0.04	0.14 ± 0.03	^{109}Cd
Pb	0.43 ± 0.08	0.38 ± 0.07	1.7 ± 0.15	0.78 ± 0.08	^{109}Cd

Table 3
Variation of heavy metal levels ($\mu g/m^3$) during the sampling period

Element	Fine particles (0.4 µm)	Coarse particles (8 µm)	Source
Ca	0.033–4.150	0.091–3.975	^{109}Cd
Mn	0.001–0.034	0.004–0.089	^{109}Cd
Fe	0.094–0.360	0.232–1.580	^{109}Cd
Cu	0.007–0.069	0.130–1.174	^{109}Cd
Zn	0.008–0.072	0.007–0.049	^{109}Cd
Br	0.008–0.098	0.007–0.060	^{109}Cd
Pb	0.055–0.419	0.031–0.465	^{109}Cd

Variations of Ca, Mn and Zn over the sampling period for the two particle sizes show the same pattern with concentration values as follows: Ca, (0.03–4.15) $\mu g/m^3$ for both filter sizes; Mn, (0.001–0.034) $\mu g/m^3$ for fine and increases by factors of 2–3 for the coarse; Zn, (0.007–0.072) $\mu g/m^3$ for both filter sizes. A significant increase by factors of 3 for Ca, 7–10 for Mn and 5–7 for Zn for the month of February–March, 1994, is noted (Figs 2, 3, 6). This corresponds to an increase of about 3% in TSP values with the
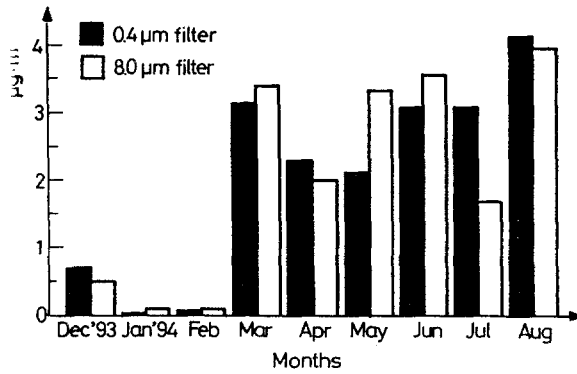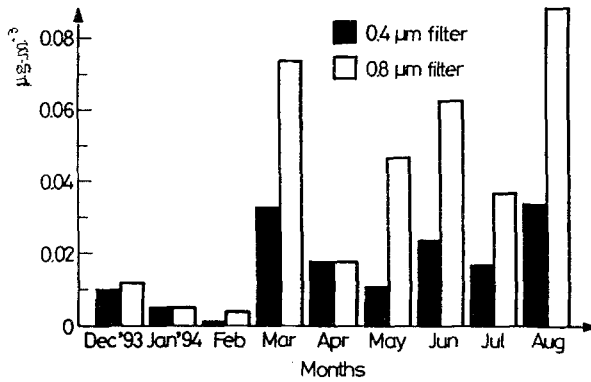
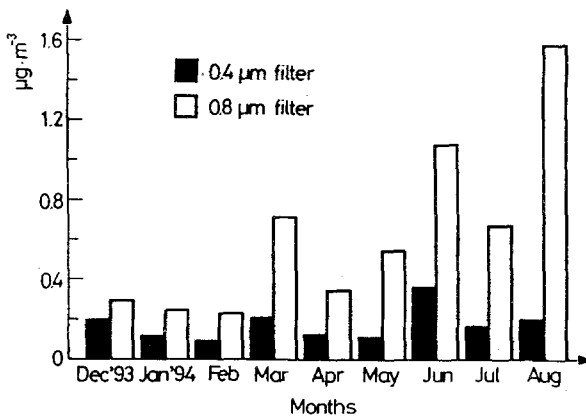Fig. 2. Variation of Ca
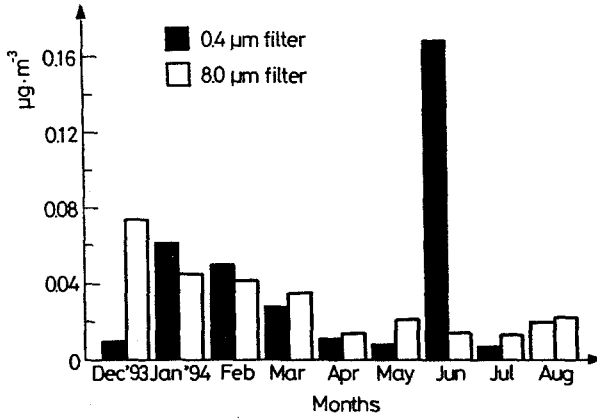

Fig. 3. Variation of Mn
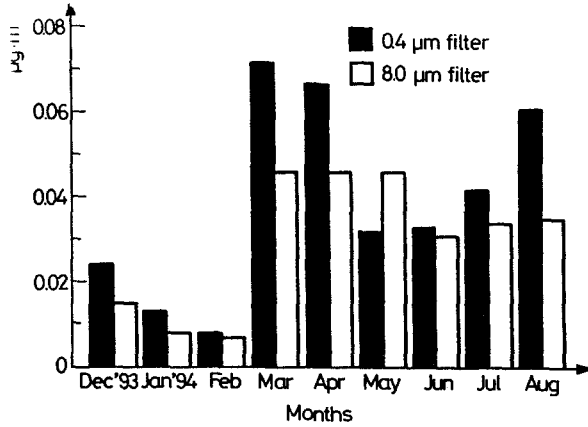

Fig. 4. Variation of Fe

Fig. 5. Variation of Cu
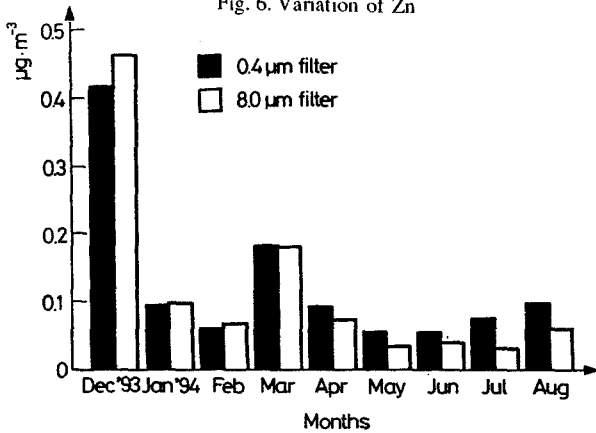
Fig. 6. Variation of Zn
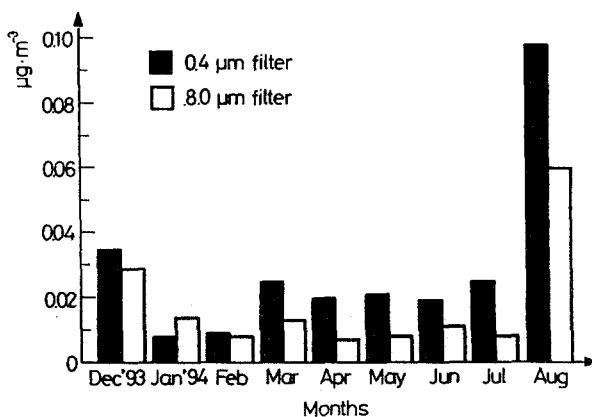
Fig. 7. Variation of Pb

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Fig. 8. Variation of Br

following meteorological conditions: easterly winds (67–112.5 degrees), constant temperature 20 °C, and increasing humidity 60% that reached a maximum value (73.4%) in May 1994. Fe exhibits the same pattern as, Mn (Fig. 4). The variations with time for most of the heavy metals follow a similar trend throughout the sampling period which indicates that their origin is most likely the same and possibly relate to the earth crust.[13]

The variations of Cu and Pb, indicate considerably high values at the start of the sampling (0.07 and 0.4 $\mu g/m^3$) for both filter sizes, respectively. This reduces to average values of 0.01 $\mu g/m^3$ and 0.05 $\mu g/m^3$ at the end of the sampling period. The trends (Figs 5, 7) for the two elements are similar, becoming negative at the end of the sampling period. This is related to the same production mechanism of these elements in the atmosphere since the average rainfall is too low to be the dominant process in the removal of particles. However, the TSP value is maximum in April/May 1994 during which the easterly winds were blowing at 2 knots.

Variations of Br for both fine and coarse filters is constant (0.02 $\mu g/m^3$) for most part of the sampling period upto July (Fig. 8). It then increases by a factor of 5 in August during which time there are low TSP values (10 $\mu g/m^3$) in the dry period with relative humidity 70% and moderate wind speeds at 9 knots.

Conclusion

The results of analysis show that there are two classes of pollution sources impacting at the sampling site: (a) Fe, Ca, Mn and Zn whose origin can be crustal, and (b) Cu, Br and Pb (anthropogenic).

Various activities that contribute to suspended particulate matter in the air are identified as those due to: cutting of trees, construction, industrial and dust blown from unpaved roads. The TSP values during the sampling period at the Kenya Meteorological Department vary between 10 to 50 $\mu g/m^3$ for both filter sizes with the variation of heavy metals as shown in Table 3.

Comparison of this work with previous studies,[2,3,5] indicates that the TSP values increased with increasing wind speed but decreases with reducing relative humidity (Fig. 1). However, the TSP values have over the past two years remained constant.

The Pb level in the aerosols is below the World Health Organisation[11] recommended levels (0.5–1.5 $\mu g/m^3$). The source of Pb and Br is due to vehicular emissions since those two form the main additives of our gasoline. It is therefore important that laws pertaining to exhaust vehicle emissions and compositions are enacted and enforced in the country to make sure that road worthy vehicles are being used. There is also need to reduce the Pb levels in our gasoline while the policy makers and urban planners need to be sensitized on air pollution issues in order to ensure low pollution levels for sustainable development.

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