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WORKPLACE MONITORING AND OCCUPATIONAL HEALTH STUDIES IN KENYA USING NUCLEAR AND RELATED ANALYTICAL TECHNIQUES

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HEAVY METAL ANALYSIS OF SUSPENDED PARTICULATE MATTER (SPM) AND OTHER SAMPLES FROM SOME WORKPLACES IN KENYA

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SUMMARY

Air pollution studies in Nairobi are indicating a rising trend in the particulate matter loading. The trend is mainly attributed to increased volume of motor vehicles, the physical change of the environment, agricultural and industrial activities. In this study, total suspended particulate matter sampling at the Nairobi industrial area and inside one workplace are reported. Included also are the results of analysis of water samples and effluents collected from a sugar factory, a tannery, and mercury(Hg) analysis in some beauty creams sold in Nairobi.

The samples were analysed for heavy metal content using Energy Dispersive X-ray Fluorescence (EDXRF) while the suspended particulate matter (SPM) concentrations were determined by gravimetric technique. Total reflection x-ray fluorescence(TRXF), atomic absorption spectrophotometry and PIXE analytical techniques plus the use of Standard and Certified Reference Materials(SRM's and CRM's) were used for quality control, analysis and evaluation of the accrued data.

Air sampling in the industrial area was done twice(Wednesday and Saturday) every week for a period of two months(November and December, 1996) and twice monthly for a period of six months (January-June 1997). Each sample covering approximately 24 hours, was collected using the 'Gent' Stacked Filter Unit (SFU), for day and night times. The SPM were found to vary from 16 to 83 mgm^{-3} during the sampling period.

The analysis of dust collected inside a workplace showed that there was poor filtration of the air pumped into the building and that there was a need for improvement of the air conditioning unit plus reduction of emissions from a neighbouring tyre factory.

Beauty creams analysed showed that there is some mercury present in significant amounts (0.14 - 3.0%). The results of these mercury levels are presented for various brands of cosmetics sold in some market outlets in Nairobi. The health implications on the presence of mercury in some of these beauty creams is also discussed.

The presence of sulphur(0.9 - 439 μg/ml) in the water samples from the River Nyando showed that waste from the factories was certainly affecting the water quality of the river. These high levels were registered at a waste treatment pond in the factory. Heavy metal analysis of the water samples collected from River Nyando along the sugar and agro-chemical food industries showed phosphorus and lead(Pb) were below detection limits which ranged from 30-180 μg/ml and 30-150ng/ml respectively. The occurrence of these high levels of sulphur during some sampling visits, suggests some random release of industrial wastes into the river and poor effluent control measures by the industries. Other parameters affected by the industrial wastes included the conductivity, salinity and BOD.

From this study, it is evident that industrial activities and some of their products, motor vehicles and the physical change of the environment are contributing significantly to environmental pollution in Kenya. Particulate matter loading and lead(Pb) levels are found to be higher than those from a previous studies. Whereas it is difficult to pinpoint the exact cause of these increases, the increase in motor vehicle volume, worsening state of our roads, lack of an effective inspection and maintenance programme of motor vehicles and industries in the country, lack of enforcement, supervision and implementation of the Kenya Factory Act provisions, are some of the major causes of this increase. There is therefore a great need for further studies geared towards epidemiological investigations especially among the factory workers, the children and the elderly.

1.0   INTRODUCTION

Cases of occupational asthma, byssinosis, silicosis and asbestosis have been reported in industrial workers (battery manufacturing, cement production, mineral processing) in Nairobi, Athi River, Thika and Mombasa Towns [Kahenya, 1996]. As a result, workers and residents who live near some of these industries have suffered a decline in their standard of living. A number of previous studies have also been done on air pollution [Gatebe and Kinyua, 1994; Muriuki, 1995; Gatebe et al., 1996], water and industrial wastes [Kinyua et al., 1990a; Kinyua and Pacini, 1991; Odhiambo, 1997]. Some recent studies [Kahenya, 1996; Kenny, 1996] have revealed that some occupational diseases are becoming a growing problem in Kenya because of the rapid rate of industrialization coupled with ignorance of the dangers caused by lack of cleaner production practices by some of the local industries.

Pollution of the atmosphere affects the lives of millions of people in all parts of the world, especially those living in large industrialized cities with heavy motor vehicles [Suess and Craxford, 1976; Schwela, 1997]. The World Health Organization lists some of the major environmental problems of urban and industrial areas and their surroundings as: unpleasant fumes and odours, reduced visibility, injury to human health and crops, damage to property by dust and corrosive gases.

In Kenya pollution from motor vehicles especially in the contribution of total suspended particulate matter (TSPM) has become significant only in the urban conditions where there is high traffic density. Lead(Pb), emitted by the motor vehicles, is added in petrol($\tilde{}$ 0.4g/L) as tetraethyl lead to improve combustion characteristics of the petrol air mixture in engines of motor vehicles[Gatebe, 1996]. This increases efficiency of engines with higher compression ratios. Most of this lead is emitted as lead oxide in the exhaust fumes and some of it becomes airborne. The airborne dust can then enter the lungs where it is absorbed into the body.

In Nairobi, like in many other cities in developing countries, there exist gross pollution which is clearly detectable by senses [Lalor et al., 1993]. Motor vehicles have been on the increase over the last few decades and it is suspected that this is accompanied with an increase in levels of motor vehicle pollutants [Gatebe, 1996]. Recent studies have shown rising trends in SPM in the city [Gatebe et al., 1996]. However, the contribution of the SPM arising from motor vehicles has not been effectively quantified.
Therefore, it was the aim of this project to sample from the Nairobi industrial area and various workplaces, the suspended particulate matter, analyse it for the heavy metal content and hopefully begin providing assessment data for future epidemiological case studies. The study is also meant to sensitize the authorities and employers in these industries on the dangers posed and also to suggest precautionary measures that can be taken so as to alleviate environmental degradation by way of cleaner production practices.

1.1 Site descriptions

(a) Nairobi Industrial Area

The Nairobi Industrial Area, is shown in the enclosed map(Fig. 1). It is 1798m above mean sea level. The wind directions are mainly easterlies while the atmosphere is neutrally stable. Air sampling at this site is for the period November 1996 - August 1997 and is still going on. This site is located some 13 km from the city center and to the south eastern side of it. It is in the main industrial area of Nairobi. Surrounding it are residential estates of high population densities particularly to the western and north-eastern sides where there are also two main soccer stadiums within ⁓ 3km. The Jomo Kenyatta International Airport is approximately 5km to the south-western side of this site. It is difficult to give an estimate of the population density around this site, since the information was not available by the time of compiling the data. However, a clever guess can put the density to be around 25000 persons per kilometre.

Within this area are also found various industries (metal, chemical, food processing, etc.). The effluents from 16 industries, two sewage treatment works and various sections of the Nairobi and Athi Rivers have previously sampled and analysed over different periods [Njuguna, 1978; Kinyua et al., 1990a; Kinyua and Pacini, 1991; Kinyua et al., 1997]. Sample collection and preservation was carried out as set by UNEP (1987). Polyethylene containers were used to minimize trace metal contamination.

(b) Voucher Processing Workplace

The Voucher Processing Unit Centre is a modern three storey building for some banking activities. The first two floors have several computer hardware and installations used for processing of the bank's financial transactions. These facilities became operational in March 1997, though they had been installed in January 1997.

The top floor of the building only houses the main air conditioning unit for the Centre. The air conditioner has inlet ducts located on the same side with the diesel power generator exhaust whose outlets face the Prisons Staff Quarters. The Avon Tyre Factory bay and an unpaved road passing next to the premises including other industrial activities are the main neighbours (Figure 2).
On each floor, the rooms in the Centre are separated by partitions of hardboard where computer terminals and peripherals have been installed. These rooms are ventilated, air conditioned and fitted with smoke detectors. The Centre has a back-up power supply from a diesel generator, located on the ground floor. The generator was used continuously in February to May 1997 before an appropriate transformer for the mains supply was installed. For most of the day, the wind direction in Nairobi is north-easterly [Gatebe et al., 1996].

Next to the Centre is the Industrial Area Prisons Department which occasionally burns its rubbish at a site close to the air inlets ducts of an auxiliary air conditioning unit which is ⁓ 5m high above the ground level. Avon Industries, a tyre manufacturing company is located adjacent to this building separated by a car park. At the time of our visit, the building floors had been cleaned by blowing and sucking by use of a vacuum cleaner. The aim was first to characterize the dust collected by use of heavy and light elemental contents and if possible, pinpoint the dust origin and also to recommend to the client the ways to eliminate this problem so as to protect the workers and the sensitive equipments installed. After rectification of this problem, the next exercise has been to sample the air particulate levels inside and outside this building by way of a portable PM-10 system recently borrowed from Schonland Research Centre for Nuclear Sciences, University of Witwatersrand, Johannesburg, South Africa. This campaign for air particulate monitoring in this building is still going on.

(c) Sugar, Food and Chemical Factory

This site is at Muhoroni which is about 400 km from Nairobi in western Kenya. It is located near Lake Victoria in the sugar belt of Kenya along the River Nyando where a lot of sugar and other agro-chemical based industries have been built. Four sampling points were selected (Fig. 3).

2. SAMPLING

(a) Total Suspended Particulate Matter(TSPM)

Sampling of SPM was done using a 'Gent' Stacked Filter Unit [Maenhaut, 1993] and as previously described [Gatebe et al., 1996]. Nucleopore filter membranes (0.4mm, and 8mm) were weighed in an air conditioned laboratory controlled at 50% relative humidity and 20°C. A ^{241}Am a-emitting source (5mCi)

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. Before the start of each sampling exercise, the SFU was properly cleaned with ethanol to remove any particles which may have previously embedded inside. Filters were handled with care using plastic tweezers to avoid grease from fingers and heavy metal contamination. Information recorded was: (i) volume of air sucked by the pump and (ii) average weather conditions. During the sampling, the sampler was run at flow rate of $1m^3$/hour for 24h sample collection ($24m^3$).

(b)   Voucher Processing Workplace

A total of 14 samples were sampled all together. Four(4) were collected on 7th August, 1997 and nine(9) samples on 15th August, 1997. Eleven(11) of these were cotton swaps that had been wiped on surfaces which had accumulated dust. The swaps were from the computer peripherals, the furniture, air inlet ducts, car park pavement and at the main air conditioner radiator. The Server Unit had also previously been sampled by the Client and a sample submitted to the Institute of Nuclear Science for analysis. This sample was reportedly obtained before the rooms had been cleaned since January 1997.

Sample   Description/Colour

A   Sampled on cotton swap from the top of the monitor in thecomputer server room by the client on 18th July 1997 (black).

B   Collected on cotton swap from the top of a cabinet in the computer server room on ground floor(black).

C   Collected on cotton swap from the top of a cabinet in the computer server room on ground floor (black).

D   Collected on cotton swap from the top of the door entrance to the computer server room on ground floor(black).

E   Collected on cotton swap from an air conditioning room on top floor of the building(brown).

F   Collected on cotton swap from the top of the router cabinet in the server room (black dust).

G   Mixture of soil and a tyre factory wastes sample collected on "murram road" behind Avon Factory (black).

H   Cotton swap dust sample from the back-up power supply generator room (brown).

I   Charred factory waste sample (black) from a smouldering "rubbish pit" next to the murram road near the loading bay of the tyre factory.

J   Cotton swap sample from the air inlet duct in the back-up power supply generator room (brown).

**L**   Soil sample from the "murram road" passing next to the Centre. Avon Factory(brown).

M   Cotton swap sample from the air conditioner room (brown dust).

N   Cotton swap sample from the radiator of the air conditioner room (brown dust).

O   Cotton swap sample from the car park pavement between Avon Industry and Centre (black).

(c)   Sugar, Food and Chemical Factory

Four sampling points were selected. Sampling was done for two weeks and 15 samples collected and analyzed for BOD, DO, TDS, hardness, salinity, conductivity, pH, and heavy metals by TXRF technique. After a visit to the factories and survey of the points of discharge and waste treatment ponds, sampling points were established as shown in Fig. 3:

MUSCO

AGRO

Water treatment ponds

(A1,B1,C1)

1

2

(A2,B2,C2)

4

(A5,B5,C5)

3

(A3,A4,B3,B4,C3,C4)
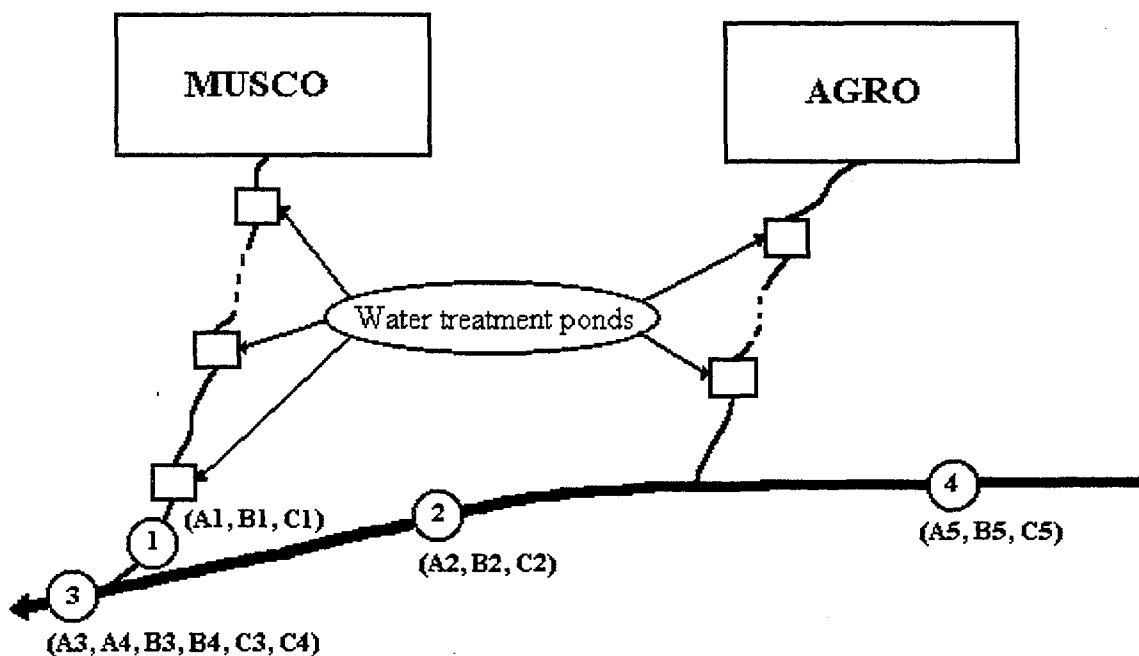
Figure 3. Sampling points in the study

Point 1 at the outlet of the last (ninth) waste treatment to determine its efficiency. Samples A1, B1 and C1 were taken at this point;

Point 2 at a distance from the Agro-Chemicals and Food Factory on the downstream but before that of Muhoroni Sugar Factory. This point was established to take

care of the waste discharged by the Agro-Chemicals and food factory. Samples A2, B2 and C2 were taken from this point;

point 3 at the discharge point of Muhoroni Sugar Factory. Samples A3, A4, B3, B4, C3 and C4 were taken from this point;

Point 4 at about 1/2 km away from the discharge point of the Agro-Chemicals Factory upstream. Samples A5, B5 and C5 were taken from this point.

Water samples were collected using one litre polyethylene plastic bottles, which had been thoroughly washed with water and 10 % nitric acid then rinsed with copious amounts of double distilled water [Maina et al., 1997]. In the field, the water bottles were washed with the water being sampled before actual samples were taken. The water bottles were immersed closed then opened at a depth of about 20 cm from the surface to avoid contamination by surface debris [Maina et al., 1997].

(d)   Beauty Cream Samples

Samples (n=100) of beauty creams were bought randomly from various retail shops in Nairobi and its environs [Kinyua et al., 1996]. Each sample was under its normal package/protection cover and suffered no atmospheric exposure that would lead to contamination and deterioration. Each sample was squeezed into a clean beaker then heated on a water bath at 40-50°C until melting was complete. The melt was then poured onto a 2.5 cm diameter Mylar (Spectro - Film grade: Somar INC., USA) supported on aluminium ring [Kinyua et al., 1994] so as to acquire the configuration of a homogenous pellet ($0.3g/cm^2$) when cooled. No other physical and/or chemical treatments were applied to the sample.

The EDXRF system utilized in this analyses has previously been described [Kinyua, 1982]. It consists of 28 mm^2 x 5 mm thick Ortec Si(Li) detector with beryllium window thickness of 25 μm, a Canberra amplifier/pulse processor with pile-up rejector Model 2020, and a Canberra S100 PC based multichannel analyzer system. The detector resolution (full width at half maximum-FWHM) was 190 eV at Mn K_a line at 5.9 keV, while the pulse shape time constant was 10 μs. The excitation source was [109]Cd (20mCi) with a run time of 300 seconds.

The spectra data deconvolution was by AXIL based software [IAEA, 1995], while quantitative analysis was by QAES Software [Kump, 1993]. The detector system was calibrated using an oil standard

reference material - NIST-SRM-1634b and some in-house standards for L-lines. Calculation of the mercury concentration in the samples was based on intensity recorded (I), being taken as equal to a product of sensitivity (S), concentration of a given element (C), absorption coefficient (A), and enhancement factor (E) [Kump, 1993]. For mercury, enhancement is absent (E=1) since there is no additional excitation of mercury by other fluorescent radiation emitted by other elements present in the sample. The absorption correction factor was measured experimentally by use of pure target of molybdenum, whereas the sensitivity curve was generated from the use of the oil standard reference material and in-house standard for other L-lines which were not present in the oil standard. The intensity (area under the mercury peak) was read from the spectrum fitting by AXIL.

(e)   Nairobi Industrial Effluents

A recent study [Kinyua et al., 1997] analysing water samples collected on the up-and-down streams of a tannery factory discharge point into Kamiti river has been done. The heavy metal analysis was done by TXRF as previously explained [Korir, 1997] while BOD and COD parameters were done as per the standard method for the examination of water and waste water [Rad et al., 1975]. Sample collection, storage and preservation was carried out as set out previously [UNEP, 1987]. Polyethylene containers were used minimize trace metal contamination. Sample preparation for analysis was carried out within 48 hours.

3.   SAMPLES ANALYSIS

3.1   Main Analytical Techniques used

a)   Energy Dispersive X-Ray Fluorescence (EDXRF)

The EDXRF system has previously been described [Kinyua, 1982]. The samples were irradiated for 3000 seconds and the spectra data were stored in a computer. Spectra de-convolution and fitting was carried out by AXIL (Analysis of X-ray Spectra by Iterative Least-Squares Fitting) modular program of the Quantitative X-ray Analysis System (QXAS) [IAEA, 1995], while quantitative analysis was by a software for Quantitative Analysis of Environmental Samples (QAES) [Kump, 1993]. Quality control assessment of the technique was done by analysis of standard reference material from National Institute of Standards and Technology (NIST), SRM 2676d.

b)   Total Reflection X-ray Fluorescence

Sample preparation

The system used for this work is as described previously [Korir, 1997]. One ml of each sample was pipetted onto a clean vial and 1 μg of cobalt per ml of sample was added as internal standard. The content of the vial was mixed thoroughly by shaking and after which 10 μl was pipetted on a cleaned sample carrier. The samples were seen to spread to about 6 mm in diameter. The sample substrate liquid was then dried in a soft vacuum at room temperature (23 $^\circ$C). For each sample, 3-4 replicates were measured.

Preconcentration of water samples

The pH of 100ml of the sample, with 10 μg of Co internal standard and 5 μg of Ni added as a carrier, was adjusted to between 5 and 6. 10 ml of freshly prepared 2% NaDDTC solution was added and stirred for 15 minutes. The precipitate formed was filtered on millipore filter of porosity 0.4 μm. The filter substrate formed was dissolved in 1 ml of MIBK solution into a clean container. 10 μl of the solution was spiked onto each of the clean sample carriers, dried and analysed.

Instrumentation

The analysis was carried out using the Vienna Prototype TXRF Module attached to the line focus of the Type D Housing of Mo target water cooled Siemens Model FK 60-04 X-ray tube. The high voltage generator used was the Kristalloflex 710H from Siemens with maximum 53.5 kV and current 40 mA. The x-ray detector used was Canberra Si(Li) Model 2008 of resolution 174 eV(Mn-K$_a$ line), active crystal

volume of 30 mm^2 and thickness 5mm. For this study, the x-ray tube used was operated at 40 kV and 20 mA. No other extra spectral modification of the Mo primary beam was done due to the low beam intensity. The TXRF module was optimised for the Mo-K lines with the cut off achieved at 20.0 keV. The angle of incident with the sample used was about 0.6 mrad. The counting dead time for most samples

averaged 1%. X-ray spectra were collected for 2000s in MCA emulation software - S100 from the Canberra. The quantitative analysis was done with the analysis package, QXAS[IAEA, 1995] after calibration of the spectrometer using a set of multi-element standard solutions with Co as internal standard [Kregsamer, 1995]. The sample carriers used were the suprasil discs, 30 mm in diameter and 3 mm thick.

c)   Gravimetric

The fine and coarse fraction mass concentrations were obtained through gravimetric measurements of the nucleopore filter membranes with 1 mg sensitivity (Ainsworth, Type 24N) weighing balance. Before weighing, the filters were equilibrated for 24 hours at 50% relative humidity and $20°C$ temperature. Electrostatic charges were controlled by use of ^{241}Am radioactive source($5\mu Ci$). The filter membranes were then weighed before and after air filtration.

d)   Carbon and Sulphur Analysis

Carbon and sulphur contents in the cotton swap samples were analysed using a Carbon-Sulphur analysis system (CS-244- LECO Corporation, USA). The system used consists of :

(i)   an induction furnace -to oxidise the carbon and sulphur in the samples to CO_2 and SO_2 at high temp ($500°C$);

(ii)   measurement unit : for CO_2 and SO_2 detection and determination of sample weight;

(iii)   control console: a microprocessor based instrument pre-programmed for measurements of C and S after calibration with standards. The accuracy and sensitivity of the system is $\pm5\%$ for levels $<0.1\%C$ and $\pm2\%$ for levels $>0.1\%$ C.

3.2   Techniques used for Quality Control and Intercomparison with EDXRF Results

a)   Total Reflection X-ray Fluorescence (TXRF)

The TXRF system used is as described above. Standard reference materials, water and other digested samples were prepared for analysis as previously discussed [Korir, 1997].

b)   Atomic Absorption Spectrophotometry (AAS)

The AAS unit used in this work as previously been described [Jumba, 1980]. It is a Perkin Elmer Model 2380 a microprocessor controlled AAS, which measures the concentration of metallic elements and provides integrated readings in absorbency and concentration. For this work, intercomparison and verification of results of the mercury levels in beauty creams, a few of the samples were extracted and analysed using an alternative technique as previously described [Wandiga and Jumba, 1982]. Aliquots (0.5g) were digested first with H_2SO_4 (1 hr) and then 6% aqueous potassium permanganate(2 hrs). The excess permanganate was destroyed with hydroxylamine and the aqueous extract analysed by flameless cold vapour atomic absorption spectrometry (AAS) - Pye Unicam SP 90A, at 253.7nm. The detection limit obtained was better than 4 ng.

c)   Particle Induced X-ray Emission (PIXE)

Ten samples were analysed using a tandem accelerator facility at Schonland Research Centre for Nuclear Science, University of Witwatersrand, South Africa. The samples which had earlier been analysed with EDXRF, were cut into an area of $2.7cm^2$ using a punch. A Proton beam (collimated with a rectangular collimator) with an energy of 3.2 MeV, and a beam current of 10nA was used. Irradiation times were 600 seconds. The PIXE system was calibrated by a large number of Micromatter Standards (mono and bielemental) of known area density (5% uncertainties certified). The fitting of the x-ray spectra and quantitative analysis were performed using the AXIL-PC software and WITS-HEX [Lipworth et al., 1993].

4. RESULTS AND DISCUSSION

4.1 Quality Control Measurements

4.1.1 EDXRF and PIXE Analysis of TSPM and SRM Materials

For both PIXE and EDXRF analytical systems, the detection limits were based on three sigma criterion [Wobrauschek , 1995]. Detection limits for PIXE are typically $5ng/m^3$ for elements in the range $13 < Z < 22$ and 0.4 ng/m^3 for elements with $Z > 23$. These detection limits were calculated based on a sampling flow rate of 20 litres per minute, 12 hours of sampling and irradiation time of 600 seconds. Table I shows the analytical results of SRM-2676d and the detection limit for the EDXRF based on the above criterion. Figure 4 shows the plot of EDXRF results versus the SRM values. The correlation coefficient between these two values was about 98%. Figure 5 and Table II shows an intercomparison of the analytical results of the analysis of coarse and fine filters by both PIXE and EDXRF techniques. There was some good agreement in some of the results especially the major elements such as iron. The differences noticed in some of the results are mainly due to falling of the sample material during transportation, preparation and inhomogeneity. However, the precision of the elemental concentration measurements is typically less than 10% for elements with concentration near the detection limit.

Table 1(a)   EDXRF analysis of a Standard Reference Material - NIST 2676d:
metals on filter media

Element	Expt. Value (μg/filter)	Certified Value(μg/filter)	Filter Number
Mn	16.06 ± 0.41	19.83 ± 0.38	III
Zn	82.05 ± 1.52	99.31 ± 1.77	III
Pb	26.55 ± 0.72	29.77 ± 0.61	III
Mn	10.54 ± 0.21	9.83 ± 0.14	II
Zn	55.54 ± 0.83	49.47 ± 0.73	II
Pb	17.76 ± 0.34	14.82 ± 0.26	II
Mn	2.84 ± 0.05	2.09 ± 0.03	I
Zn	13.33 ± 0.18	10.17 ± 0.13	I
Pb	10.84 ± 0.15	7.44 ± 0.10	I

Table 1(b)   Experimental Detection Limits for EDXRF

Element	Atomic Number	Detection Limits(μg/filter)	Detection Limits(ng/m^3)*
Ca	20	2.15 ± 0.21	89.5 ± 8.5
Mn	25	0.41 ± 0.03	17.0 ± 1.0
Fe	26	0.33 ± 0.01	13.5 ± 0.5
Cu	29	0.18 ± 0.03	7.5 ± 1.5
Zn	30	0.15 ± 0.02	6.0± 1.0
Pb	82	0.19 ± 0.02	8.0 ± 1.0

Nb: * - based on 24h sample collection ($24m^3$) if flow rate is $1m^3$/hour using Gent SFU
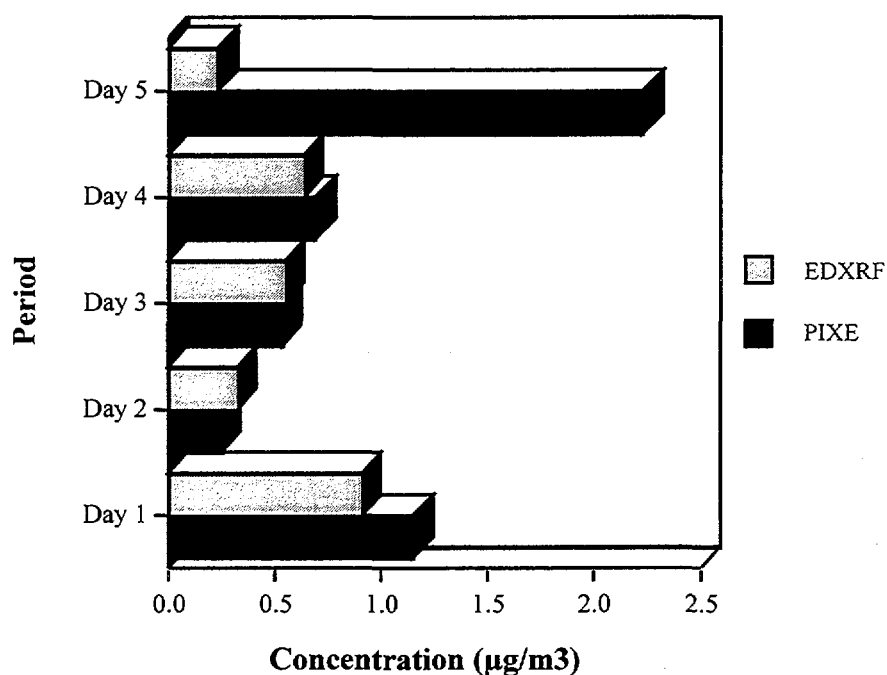
Table 2: Comparison of EDXRF and PIXE Analysis of Aerosols Samples(μg/m^3)

| Element	Fine Filter (0.4μm)		Coarse Filter (8μm)		Period
	EDXRF	PIXE	EDXRF	PIXE	
K	0.0956	0.167	0.544	0.667	Night 1
Mn	0.0629	0.014	0.0765	0.108	"
Fe	0.165	0.149	0.909	1.154	"
Zn	0.177	0.137	0.119	0.153	"
Pb	0.0741	0.047	0.0944	DL	"
K	0.187	0.075	0.517	0.317	Day 2
Mn	0.0752	DL	0.0752	0.021	"
Fe	0.137	0.061	0.322	0.247	"
Zn	0.0852	0.036	0.028	0.026	"
K	0.60	0.159	0.0305	0.229	Day 4
Mn	0.107	0.015	0.187	0.047	"
Fe	0.151	0.145	0.549	0.54	"
Zn	0.133	0.147	0.109	0.045	"
K	0.20	0.106	0.0751	0.319	Night 4
Mn	0.0678	DL	0.0619	0.064	"
Fe	0.0992	0.048	0.64	0.693	"
Zn	0.0637	0.024	0.0679	0.055	"
K	0.0221	0.068	0.409	0.072	Day 5
Mn	0.0661	DL	0.12	DL	"
Fe	0.0671	0.05	0.231	2.219	"

Nb: DL - Detection limit
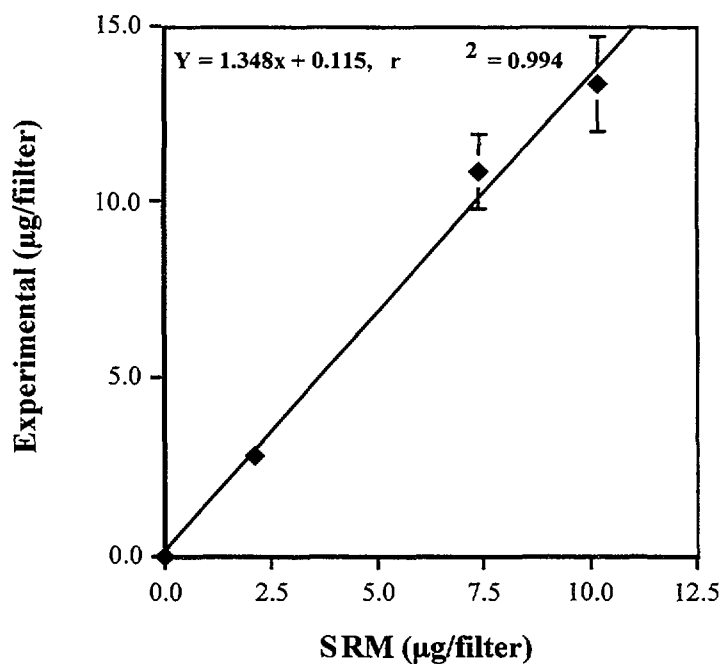
Figure 4   Comparison of EDXRF Results(Mn,Pb) with those of NIST 2676d Standard

Figure 5   Comparison of EDXRF and PIXE Results for Iron in Coarse Filter

4.1.2   EDXRF and AAS of Cosmetic Creams

The correlation between the mercury analytical results obtained by intercomparison of EDXRF and cold vapour AAS techniques was better than 95 % for the samples analysed (Fig. 6).

Y = 1.005x + 142.015, r^2 = 0.998
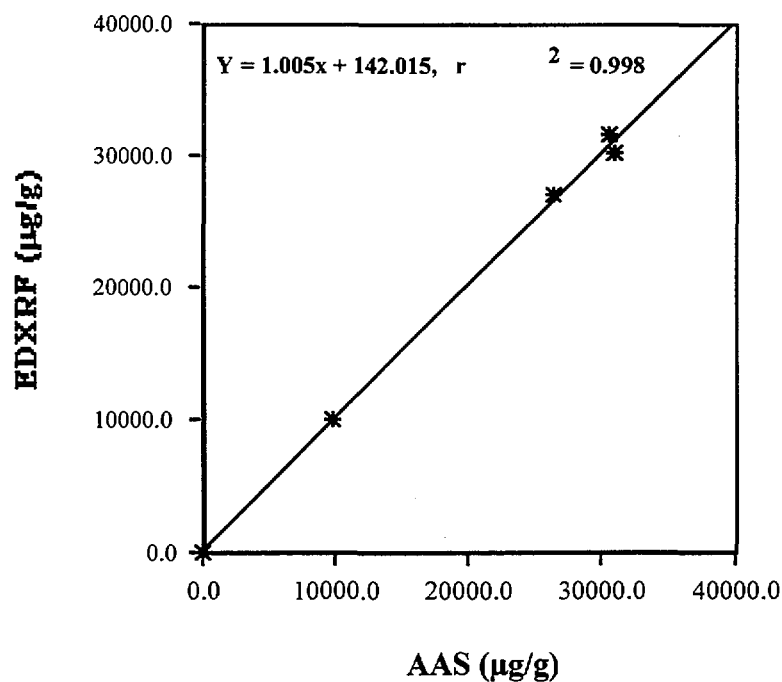
Figure 6   Comparison of EDXRF and AAS Results of Mercury analysis

4.1.3 TXRF of Standard Reference Materials and Laboratory Water Standards

4.1.3.1 TXRF analysis of Standard Reference Materials

The analysis of various standards including those from in-house preparations, are as shown below:

Table 3.   Values for Lyophilised Pig Kidney (BCR No.186)

Element	Experimental(μg/g)	Certified(μg/g)	LLD*
Mn	7.4±0.4	8.5±0.3	0.7
Fe	275±11	299±10	0.8
Cu	31.6±0.5	31.9±0.4	1.4
Zn	134±6	128±3	1.4
Se	9.7±0.5	10.3±0.5	1.4

Table 4.   Values of concentration for Chinese Human Hair (GBW 09101)

Element	Experimental(μg/g)	Certified(μg/g)	LLD*
Ca	1022±69	1090±721	2.7
Cr	3.2±0.3	4.8±0.4	0.9
Mn	3.6±1.0	2.9±0.2	0.7
Fe	71.0±5	71.2±6.6	0.8
Ni	3.4±0.2	3.2±0.4	1.3
Cu	23.0±0.8	23.0±1.4	1.4
Zn	194±5	189±8	1.5
Sr	5.7±0.5	4.2±0.1	2.4
Pb	11±1	7.2±0.7	5.2

Table 5. Concentration values in μg/g for Rye Flour (IAEA/ V-8)

Element	Experimental value	Certified value	LLD*
K	2320±191	1925±135	1.3
Ca	142±4	149±10	0.5
Mn	2.1±0.1	2.06±0.12	0.1
Fe	5.3±0.5	4.1±0.7	0.1
Cu	0.75±0.03	0.95±0.19	0.3
Zn	2.65±0.2	2.53±0.33	0.2
Br	0.31±0.1	0.38±0.07	0.2
Rb	0.55±0.04	0.48±0.07	0.2

Table 6.   Values for 'rice-unpolished'(NIES No. 10(a))

Element	Experimental(μg/g)	Certified(μg/g)	LLD*
K	1875±73	1800±80	5
Ca	100±4	93±3	3
Mn	31.3±0.7	34.7±2	0.5
Cu	7.9±0.2	3.5±0.3	0.6
Zn	24.8±0.5	25.2±0.8	0.6
Rb	4.4±0.4	4.5±0.3	0.6

Table 7. Values of concentration for Japanese Tea(NIES No.7)

Element	Experimental(μg/g)	Certified(μg/g)	LLD*
K	18850±784	18600±700	10
Ca	3131±22	3200±120	7
Mn	627±10	700±25	1.4
Ni	4.6±0.3	6.5±0.3	1.4
Cu	6.3±0.3	7.0±0.3	1.4
Zn	35.8±1	33.0±3	1.4

Table 8 Concentration values for Kale (IAEA/S636F)

Element	Experimental(μg/g)	Certified(μg/g)	LLD*
K	25909±2922	24370±1452	13
Ca	38914±4383	41060±2220	9
Mn	15.4±0.8	14.8±1.68	2
Fe	81.5±8	119.3±14.8	2
Cu	3.4±0.9	4.9±0.63	2
Zn	32.0±2	32.3±2.8	2
Br	15.0±2	24.9±2.5	2
Rb	57.3±5	53.4±5.5	2
Sr	76.4±6	75.7±29.3	1

* limit of detection

Table 9   *TXRF analysis of a In-house Water Standard*

Element	Experimental(μg)	Expected value(μg)
Ti	3.18 ± 0.04	4.0
Fe	4.25 ± 0.03	"
Ni	4.17 ± 0.03	"
Cu	3.65 ± 0.03	"
Zn	3.86 ± 0.03	"
Sr	3.43 ± 0.03	"
Pb	3.46 ± 0.05	"

Table 10 *EDXRF analysis of an In-house Water Standard*

Element	Experimental (ppb)	Expected value(ppb)
Ti	84.1± 21.5	100
Fe	125.0 ± 11.3	"
Cu	105.0 ± 8.6	"
Zn	78.7 ± 6.6	"
Pb	108.0 ± 8.2	"

4.2   Air Particulate Monitoring

4.2.1   *Nairobi Industrial Area Site*

4.2.1.1 *TSP and Heavy Metal Analysis*

Results over the eight months of sampling shows almost similar trends for all the elements Figs. 7-14. **(Please see at end of country report)** The concentration of Potassium(K), Calcium(Ca), and Iron(Fe) varies from 0.2 to 2 μg/m^3, with Ca showing a higher level than Fe and K over the entire period.

Zinc(Zn) is conspicuously high in all the months varying from 1.0 to 8 $\mu g/m^3$. This points out to presence of an industry(ies) dealing or producing Zn or it products. Comparison of these results with the ones from the suburban site(see previous CRP reports and Gatebe et al, 1996) shows higher concentration levels for most elements. This indicates some enrichment from the industries around the sampling site in the industrial area. With this data it will now be possible to sensitize the government on the need to monitor closely the impact of the industries on our air quality.

4.2.2 *Voucher Processing Workplace*

4.2.2.1 *Sample characteristics and other general observations*

(i)   Dust samples from the Computer Server room were "black" in appearance.

(ii)   Dust samples from the air conditioner located on top floor and from the back-up power supply room were brown in colour.

(iii)   The dusty "black" samples are fine powder that can easily be transported in air. However, due to the small quantities collected, these samples were not determined for their particle sizes.

4.2.2.2 *Heavy Metal Analysis*

A total of 10 elements in the samples after analysis with x-ray fluorescence method(EDXRF) are reported. These elements are: potassium(K), calcium(Ca), titanium(Ti), manganese(Mn), iron (Fe), copper(Cu), zinc(Zn), bromine(Br), lead(Pb). Tables 11 and 12 are results of these analysis.

Table 11: Relative elemental intensities($c/s/g$)

Ele	A	B	C	D	E	F	H	J	M	N	O	BL
K	-	0.45	0.23	-	0.05	0.11	0.65	0.57	0.21	0.10	0.39	0.02
Ca	1.64	2.11	1.83	0.56	0.55	0.79	1.79	1.72	0.66	0.48	1.44	0.23
Ti	0.25	0.29	0.36	0.07	0.13	0.17	0.87	0.69	0.26	0.18	0.48	0.03
Mn	0.33	0.49	0.47	0.07	0.31	0.16	2.04	1.54	0.71	0.48	1.07	0.05
Fe	4.87	9.07	10.53	2.23	7.49	4.61	43.17	31.12	13.65	10.69	23.33	0.82
Cu	0.14	0.32	0.15	0.10	0.49	0.11	0.30	0.21	0.09	0.12	0.15	0.08
Zn	1.43	2.27	2.60	0.42	2.61	1.35	2.01	1.56	2.13	0.85	2.01	0.16
Br	0.33	0.32	0.28	-	0.08	0.29	0.25	0.19	0.08	0.16	0.02	0.04
Rb	-	-	-	-	-	-	0.67	0.37	0.14	0.12	0.28	0.02
Sr	0.92	0.83	0.61	0.56	0.35	0.40	1.40	0.86	0.42	0.39	0.80	0.28
Y	-	-	-	-	-	0.10	0.44	0.30	0.10	0.10	0.24	0.03
Zr	0.66	0.78	0.92	0.13	0.93	0.44	6.77	3.85	1.76	1.36	3.15	0.06
Pb	0.43	0.36	0.47	0.15	0.14	0.27	1.00	0.60	0.26	0.33	0.44	0.06

(i)   Samples **A, B, C, D, F** (all from the Server room) have similar matrix and are from the same source.

(ii)   Samples **E, H, J, M** and **N** (from the air conditioner and generator rooms) have high levels of crustacean elements:- potassium (K), calcium(Ca), iron(Fe) as compared to the other samples. This suggests air dust as the possible source.

4.2.2.3 *Carbon and Sulphur*

(i)   Samples **G** and **I** (Table 12) contain high levels of carbon and sulphur. The values are : carbon 79% and 2.54% sulphur for sample **G** and 4.97% carbon and 0.13% sulphur for sample **I**.

(ii)   The ratio of carbon to sulphur in the samples **G** and **I** are: 38.2 and 31.1 respectively which implies that carbon and sulphur in these samples have same origin.

Table 12: Elemental concentration values in mg/g (else in %)

Element	Sample G	Sample I	Sample L
C	4.97%	79%	-
S	0.13%	2.54%	-
K	(3.4 ± 0.3)%	(0.6± 0.1)%	5.11± 0.5)%
Ca	(3.14 ± 0.3)%	(0.57 ± 0.03)%	(2.8 ± 0.4)%
Ti	(0.4 ± 0.1)%	-	(0.49±0.06)%
Mn	(0.17± 0.02)%	(0.36± 0.01%	(0.47± 0.01%
Fe	(2.7 ± 0.1)%	(0.16± 0.01)%	(4.28± 0.06)%
Cu	27.0 ± 1.0	< 10	37±4
Zn	638 ± 27	(4.9±0.2)%	218±29
Br	-	118±13	5.6±0.3
Rb	50 ± 4	7.8±0.3	69±2
Sr	216 ± 8	13.5±3	173±2
Y	27.0 ± 1.0	-	37±2
Zr	353± 23	11.2±1	527±2
Pb	62 ± 6	89±7	68±3

4.2.2.4 *Discussion*

(a)   Samples from the air conditioner room (**E, M** and **N**) and the back-up power generator room (**H** and **J**) are of similar matrix but heavily loaded with particulate matter as suggested by enrichment in the samples with iron(Fe), calcium(Ca), manganese(Mn) and potassium(K). Construction activities and unpaved roads in the area all contribute to increased dust particles in the air. Other air polluting activities include; industrial and traffic emissions [Gatebe et al., 1996].

(b)   There was no significant differences in results of heavy metal analysis of the samples collected by the Consultant and that by the Client. This in principle is an indication that the samples are of similar matrix and composition.

(c)   There is no significant reductions in the levels of heavy metals; iron (Fe), zirconium(Zr) and zinc(Zn) for samples collected from the Air Conditioner room and those from the Server room. This implies poor filtration of the air.

(d)   Carbon and sulphur in the samples seem to be of the same origin.

4.2.2.5 *Recommendations*

a)   The air filtration system in the premises is not efficient due to the following:
   i).the room entrances and exits were not properly constructed so as not to allow the dust inside.
   ii). openings on the ground floor for cable installations were not properly sealed against the dust.
   We therefore recommended a closed /or open-loop air filtration system for the premises. This system is capable of filtering out air particles sizes less than 10μm or less depending on the filter material installed (Fig.15 and 16).

b)   It was recommended that the floors in the premises be carpeted.

c)   It was recommended that some dialogue and negotiations on the possible ways and means to reduce the particulate matter in air by way of clean production practices be initiated between the bank, the neighbouring firms and relevant authorities.

4.3   Sugar, Food and Chemical Factory

4.3.1   Heavy Metal Analysis

Results of heavy metal analysis of the water samples collected from River Nyando along the sugar and agro-chemical food industries are shown in Table 13. Phosphorus and lead(Pb) were below detection limits which ranged from 30-180 μg/ml and 30-150ng/ml respectively. The presence of sulphur in these water samples was an indicator of poor effluent control measures by the industries.

Table 13. Elemental Analytical Results in µg/ml (ppm)

Sample	Phosphorous	Sulphur	Calcium	Lead
A1	DL	3.6±0.5	99±2	DL
A2	"	0.90±0.02	16±0.6	"
A3	"	1.2±0.2	18±0.1	"
A4	"	1.1±0.2	18±0.5	"
A5	"	1.1±0.3	18±0.02	"
B1	"	439±2	47±1.0	1.46 ± 0.1
B2	"	182±2.3	19±1.0	DL
B3	"	190±4.2	18±1.3	"
B4	"	259±4.7	20±3	"
B5	"	166±14	17±0.1	"
C1	"	169±5	88±3.8	"
C2	"	164±20	13±1.1	"
C3	"	434±2.2	36±2.3	"
C4	"	228±8.1	31±1.6	"
C5	"	165±13.1	13.9±0.3	"

DL* - detection limit

4.3.2 Other Measurements

Table 14 shows measurements of conductivity, pH, salinity, total dissolved solids(TDS), hardness, biochemical oxygen demand(BOD) and dissolved oxygen(DO). The pH remained relatively very basic in most of the samples analysed. However, the conductivity levels of industrial effluents(A1,B1,C1) were about four(4) times those of the river water while the salinity levels were about eight(8) times. The BOD levels of the waste from the sugar factory is about 100 times that of the river water before any industrial waste discharge while that from the agro industry is about 13 times that of the river water (A5,B5,C5). Although the river seems to recover, the industrial wastes certainly do elevate the BOD levels of the river waters. The requires constant monitoring to ensure that the limits are not exceeded.

Table 14   Results of other Parameters

Sample	Conductivity (mg/l)	pH	Salinity (mg/l)	TDS (mg/l)	Hardness (mg/l)	B.O.D. (mg/l)	D.O. (mg/l)
A5*	246	7.31	0.1	116	124	15	4.4
B5*	140	8.02	0.1	102	126	50	2.0
C5*	237	7.26	0.1	109	118	10	4.2
A2**	205	8.65	0.1	97	84	380	2.8
B2**	321	8.3	0.1	187	99	420	3.6
C2**	188	8.07	0.1	82	91	320	2.6
A1#	1344	7.30	0.7	654	184	2640	1.6
B1#	1286	9.6	0.9	715	193	2450	1.8
C1#	1256	6.9	0.9	701	203	2360	1.8
A3##	201	9.01	0.1	103	92	250	2.4
A4##	233	8.03	0.1	110	98	30	2.2
B3##	302	8.1	0.1	115	89	310	2.0
B4##	285	7.9	0.1	132	72	305	2.0
C3##	192	9.2	0.1	121	81	300	2.2
C4##	201	8.11	0.1	97	104	25	2.4

Key: *   - Samples collected before factory discharge points
        **   - Samples collected after the Agro-chemical discharge point
        #   - Samples collected after waste treatment ponds of the sugar factory
        ##   - Samples collected after the discharge point of the sugar factory

4.4 Beauty Creams

4.4.1 *Mercury Analysis*

The results of mercury analysis are shown in Fig.17. Typical spectra of cosmetic products analyzed is shown in Fig. 18. Elemental sensitivity for the EDXRF system used is shown in Fig. 19 while the absorption correction factors for mercury varied between 1.5 and 1.8 implying light matrix samples. The enhancement correction factor was taken to be 1 because no other heavy metal was present in most of the samples to additionally excite mercury L-lines.
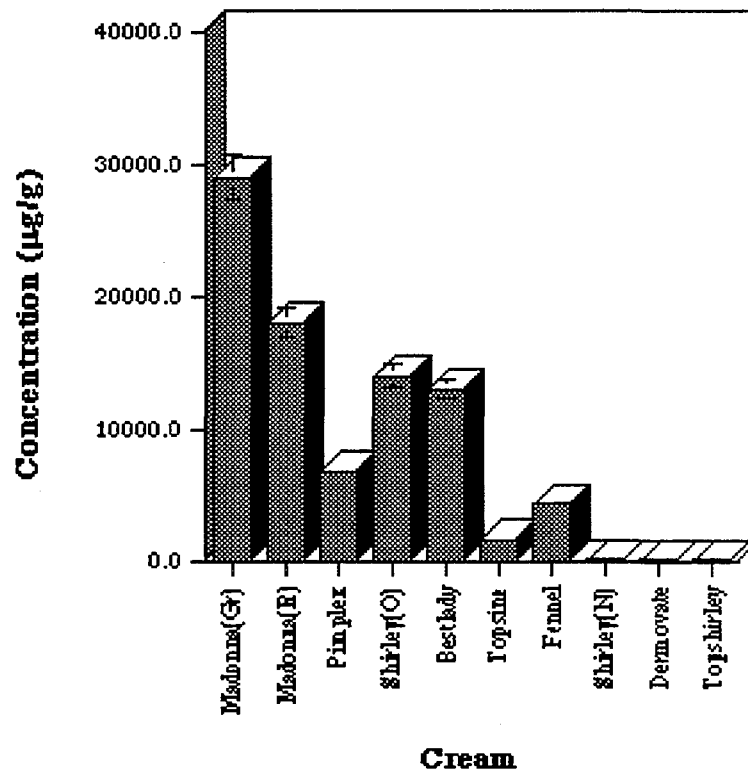

Fig. 17.   Mercury levels in Beauty Creams
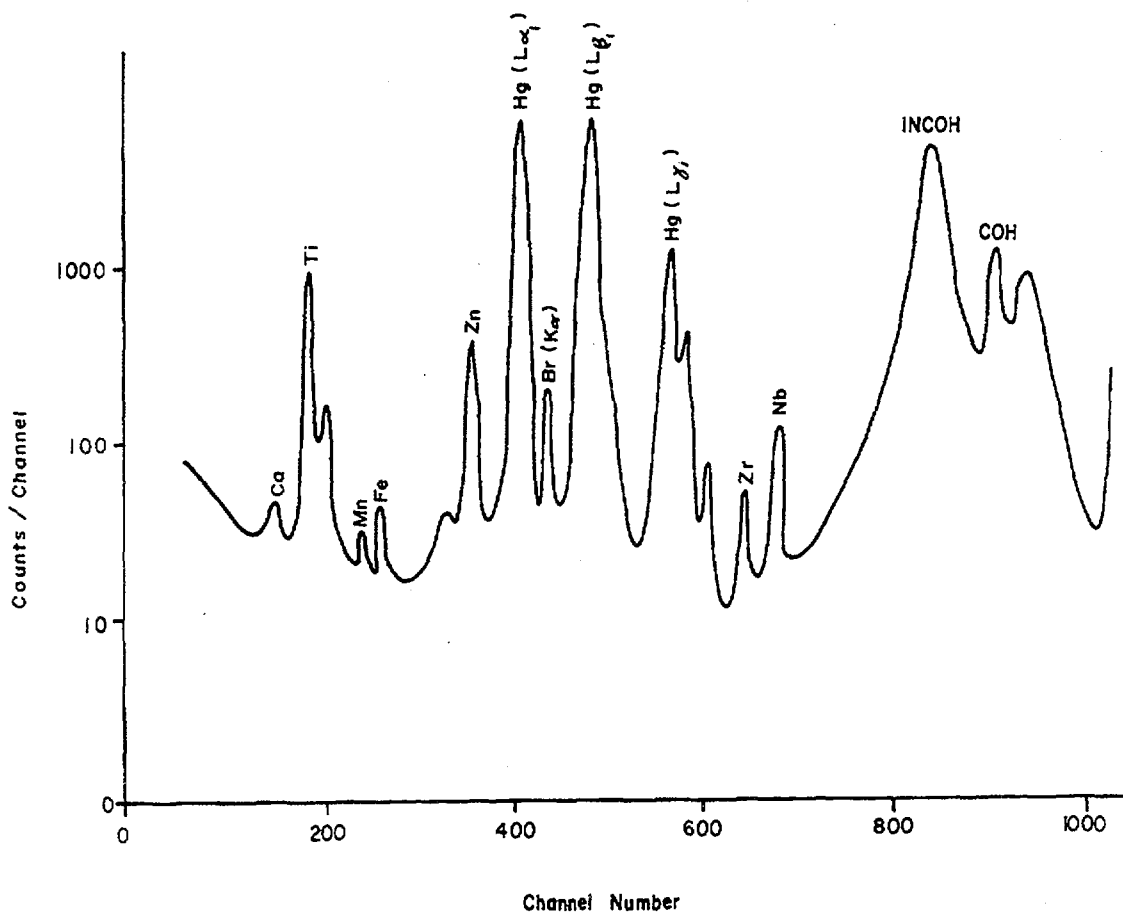
Fig. 18 Typical EDXRF Spectrum of "Madonna"(Green) Sample

$$Y = -0.000x^2 + 0.039x - 1.697, \quad r^2 = 0.912$$
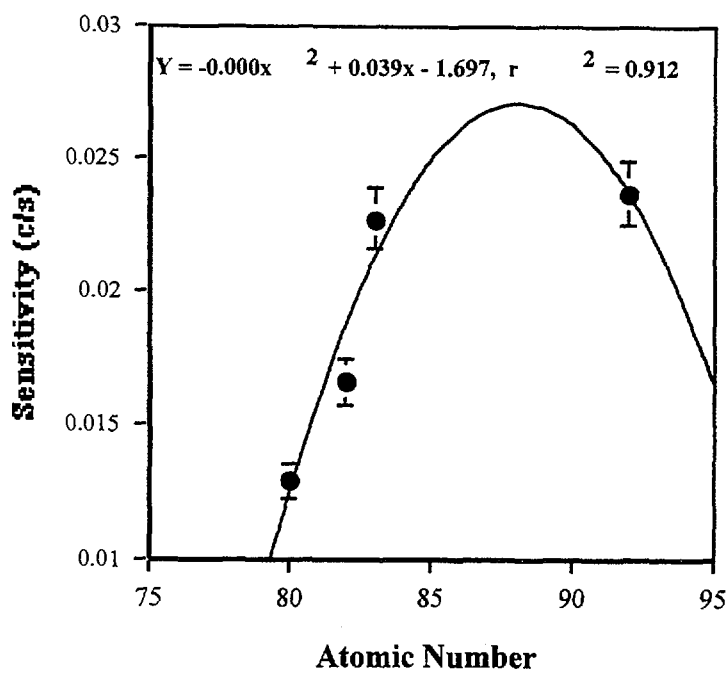
Fig. 19 Elemental Sensitivity Curve

4.4.2 Discussion

Results of mercury level measurements and analysis showed that the cosmetic cream "Madonna"(green) had the highest level (μg/g) of mercury - 29000 $\pm$ 2800 followed by "Madonna" (red) cream with 18000 $\pm$ 1700. Significant differences($p < 0.001$) in the analytical results for "Madonna" (red), "Pimplex" and "Shirley"(original) were observed for the samples bought March and September, 1995. The creams, "Shirley" (new), "Dermovate" and "Topshirley", registered values below the detection limit (3 μg/g).

Two significant findings of this study is that mercury is present in some of the beauty products being sold in Kenya. This confirms previous findings which reported levels of mercury above 1μg/g [Wandiga and Jumba, 1982]. Secondly, the level of mercury is not constant in different batches of some products bought during the sampling periods. For example, the mercury levels(μg/g) during the month of March 1995 for "Madonna"(red) was 16080 $\pm$ 1030 (n=5); "Pimplex" cream (n=5) had 4350 $\pm$ 290 while "Shirley"(original) had 18090 $\pm$ 890(n=5). For the month of September 1995, the mercury levels (μg/g) were: 20900 $\pm$ 1400(n=5), 9644 $\pm$ 630(n=5) and 10895 $\pm$ 690(n=5) respectively. The highest variation (121.7%) was for "Pimplex" cream. This has the implication on the quality control during manufacture of these products and it is possible that some products could be on sale with even higher levels of mercury than those shown in this work.

Mercury levels in some of the products analysed were above the World Health Organization (WHO) limit of 5 μg/L in human blood [WHO, 1996]. Although the levels of mercury absorbed through the skin will usually be less than the levels in the samples analysed, the health implications on the uses of some of these products need to be investigated further. This is especially with the objective of tracing the causes of the presence of mercury in nails and hair [IAEA, 1978] plus renal problems and hypertension, reported previously and attributed to heavy metals especially among the youth in this country [Kinyua et al., 1990b]. In their study involving African women in Kenya [Barr et al., 1972] attributed damaged kidneys to the effect of mercury present in the skin lightener creams used by the women. However, previous studies [Kinuthia et al., 1978] observed that there was no single etiological factor found to be of major significance in the causation of nephrotic syndrome in Nairobi. The latter authors suggested the presence of a chemical pattern of nephrotic syndrome which co-existed with haematuria, azotemia and hypertension.

The major risks to human health arise from the neurotoxic effects of mercury in adults [Bakir et al.,1973] and its toxicity to the foetus if women are exposed to methyl mercury during pregnancy [Cox et al., 1989]. Since the form of mercury present in these beauty creams is largely organic [Jumba, 1996], there is need for the local authorities to implement stringent measures to curb the sale of these products. This is more so especially when the level of mercury appear to have increased tremendously in comparison to those reported in a previous survey [Wandiga and Jumba, 1982]. Organic mercury has greater affinity for the brain, and in particular, posterior cortex as well as adipose tissue beneath the skin [WHO, 1996]. The technique developed above can be utilized for fast and regular monitoring and has the added advantage of permitting multi-elemental analysis. Other well known chemical analytical techniques take too long due to lengthy sample preparation procedures before analysis, and also require expensive and toxic reagents.

4.5 Nairobi Industrial Effluents [Kinyua, 1997]

Table 15   Results of Kamiti River Analysis (ppb unless otherwise stated)

Parameter	Upstream		Downstream	
BOD	7 mg/L		20 mg/L	
COD	28 mg/L		112 mg/L	
S	1651 ± 251	1852 ± 497	3186 ± 335	3094 ± 267
Cl	6652 ± 275	5417 ± 398	4430 ± 229	5593 ± 161
K	12826± 253	11246 ± 312	9406 ± 201	10227 ± 158
Ca	10000 ± 15	10099 ± 150	15533 ± 129	16332 ± 136
Ti	155± 15	236 ± 23	159 ± 15	119 ± 10
Cr	< 23	< 37	34 ± 10	< 23
Mn	127 ± 12	143 ± 19	687 ± 15	550 ± 12
Fe	1590± 30	2181 ± 32	3279 ± 27	2748 ± 25
Cu	40 ± 10	< 48	< 19	< 16
Zn	24 ± 7 ppb	41 ± 11	25 ± 6	23 ± 6
As	< 34	< 56	< 32	< 26
Br	42 ± 13	61 ± 20	42 ± 11	104 ± 8
Rb	< 32	< 60	< 30	< 26
Sr	91 ± 13	103 ± 25	52 ± 15	89 ± 9
Pb	< 81	< 137	< 78	< 90

CONCLUSION

The concentration of SPM varied from 16 to 83 mg/m^3, which falls below WHO 24 hour guidelines of 60 - 90 mg/m^3 [WHO, 1987]. However, these levels are higher than previous data (16-60 μg/m^3) [Gatebe et al., 1996] from a semi-urban site. The highest concentration of lead(Pb) observed during the period of study was 1.05 mg/m^3 from the 0.4 μm filter. This value falls very close to the maximum WHO guidelines of 0.5 - 1.5 mg/m^3. The equivalent value for 8 μm filter was 0.76 μg/m^3 and is also higher than our previous semi-urban data. The concentration of potassium, calcium and iron varied from 0.2 - 2 μg/m^3, with calcium registering a higher level than Fe and K over the entire period. Zinc levels remained high throughout the sampling period varying from 1.0 - 8.0 μg/m^3. This implies some presence of some industry(ies) having some zinc emissions. In general, most the elements showed higher concentrations than those levels previously recorded at the semi-urban site.

The results of analysis of the effluents from the River Nyando showed that waste from the factories was certainly affecting the water quality of the river. High levels of sulphur (0.9 - 439 μg/ml) were registered at a waste treatment pond in the factory. The occurrence of these high levels during some sampling visits, suggests some random release of industrial wastes into the river. Other parameters affected by the industrial wastes included the conductivity, salinity and BOD. This calls on the authorities to initiate some strident monitoring of industrial wastes.

Construction activities and utility of unpaved roads in the area around the Voucher Processing Centre showed that these activities did contribute to increased dust particles in the workplace. Other air polluting activities include, industrial and traffic emissions [Gatebe et al., 1996].
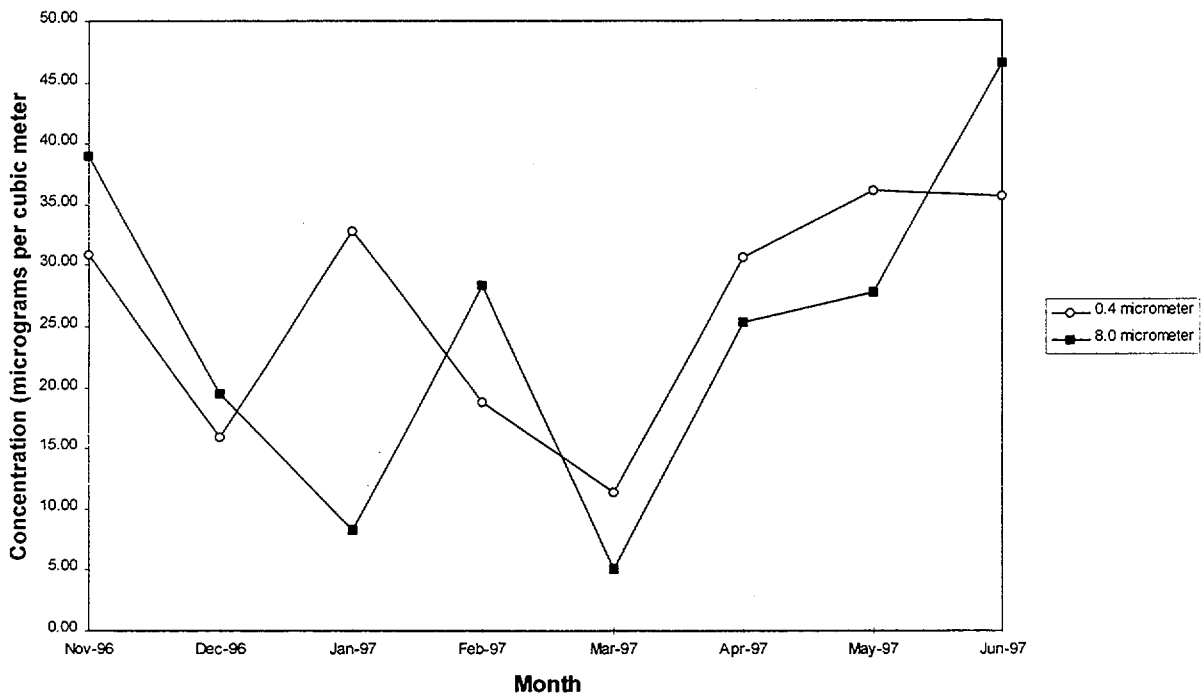
There was also no significant reductions in the levels of heavy metals; iron (Fe), zirconium(Zr) and zinc(Zn) for samples collected from the Air Conditioner room and those from the Server room. This implied poor filtration of the air. Carbon and sulphur in the samples analysed seemed to be of the same origin. It was therefore concluded that the air filtration system in the premises was not efficient due to first, the room entrances and exits being not properly constructed so as not to allow the dust inside. Secondly, the openings on the ground floor for the cable installations were not properly sealed against the dust. It was therefore recommended that a closed/or open-loop air filtration system for the premises be installed. This system is capable of filtering out air particles sizes less than 10μm or less depending on the filter membrane installed. Finally, it was recommended that some dialogue and negotiations on the possible ways and means to reduce the particulate matter in air by way of clean production practices be initiated between the bank, the neighbouring firms and relevant authorities.

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Fig. 7 Variation of SPM for 8 μm and 0.4 μm Filters

Legend:
- —○— 0.4 micrometer
- —■— 8.0 micrometer

Y-axis: Concentration (micrograms per cubic meter)
X-axis: Month

Fig. 8 Variation of Zn, Cu and Mn for 8 μm Filter

Legend:
- —○— Mn
- —■— Cu
- —▲— Zn

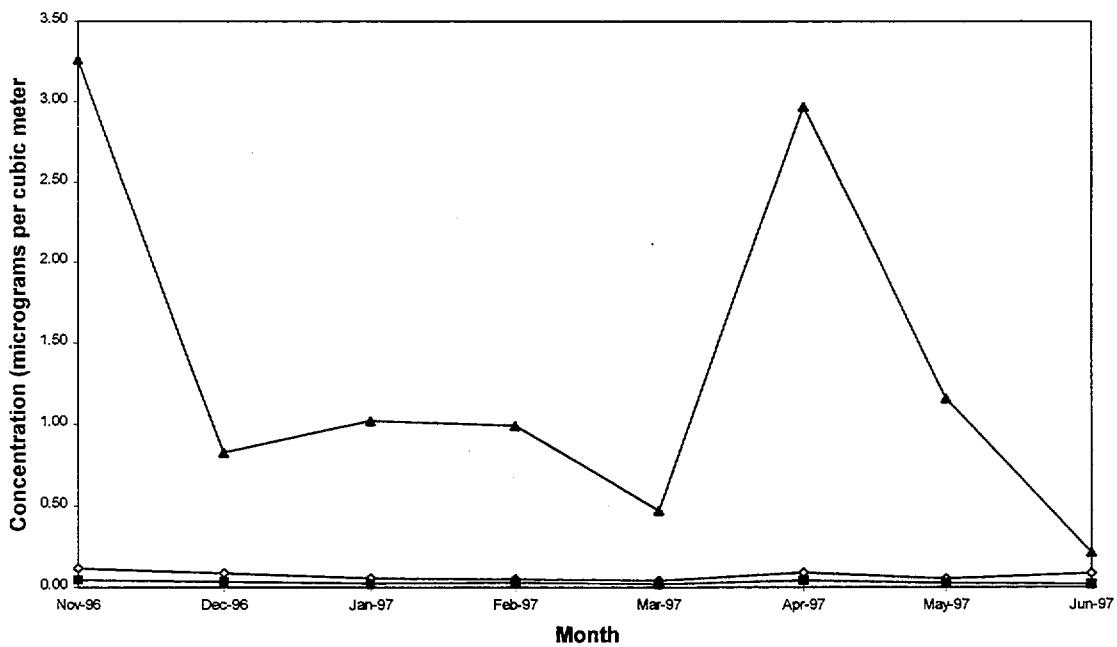Y-axis: Concentration (micrograms per cubic meter)
X-axis: Month

Fig. 9 Variation of Cu and Mn for 8 μm Filter
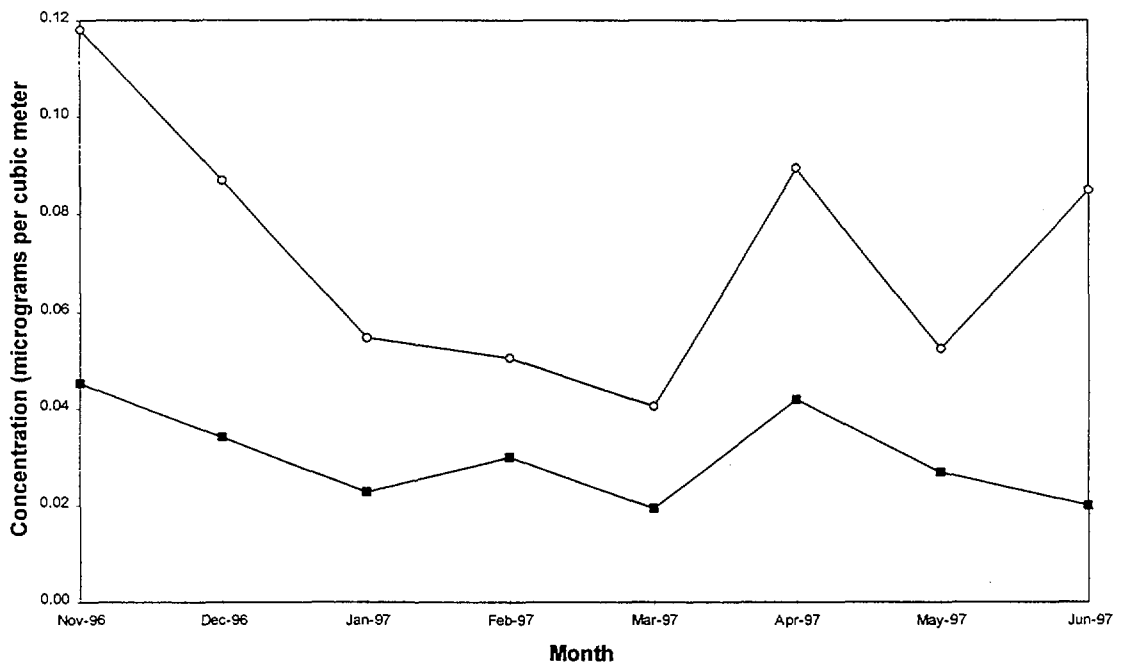
Fig. 10 Variation of Mn, Cu and Zn for 0.4 μm Filter
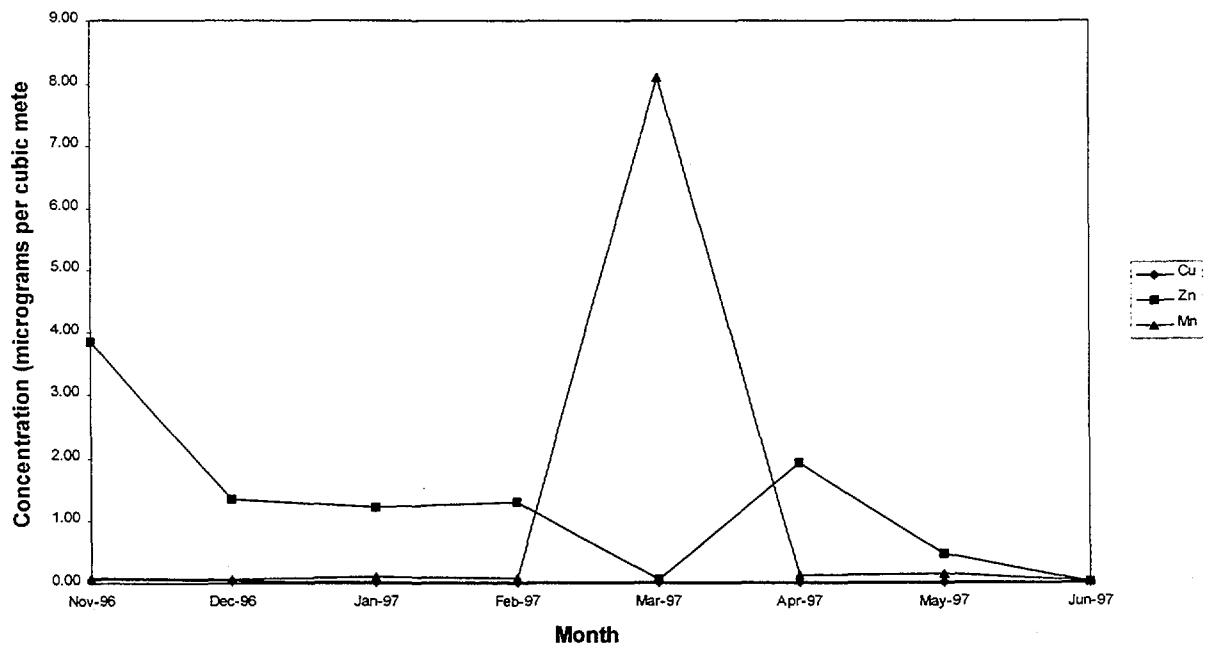
Fig. 11 Variation of K, Ca, and Fe for 8 μm Filter

Fig. 11 Variation of K, Ca, and Fe for 8 μm Filter
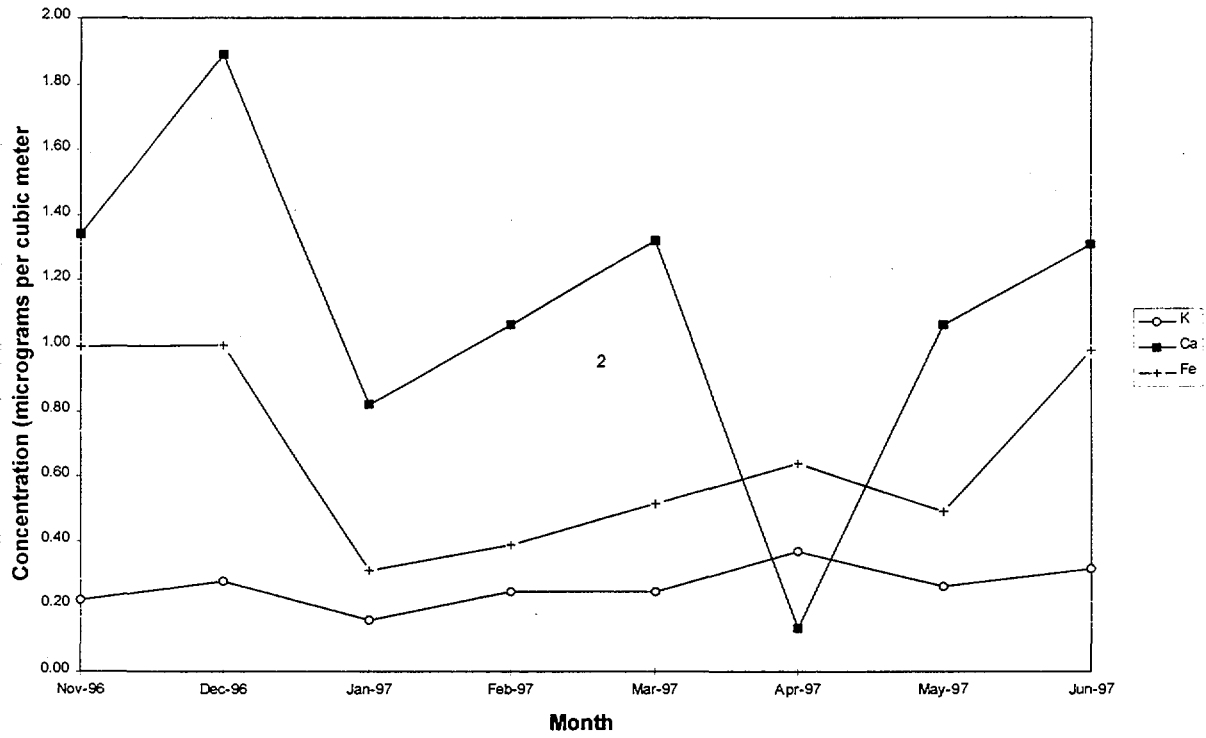
Fig. 12 Variation of K, Ca and Fe for 0.4 μm Filter

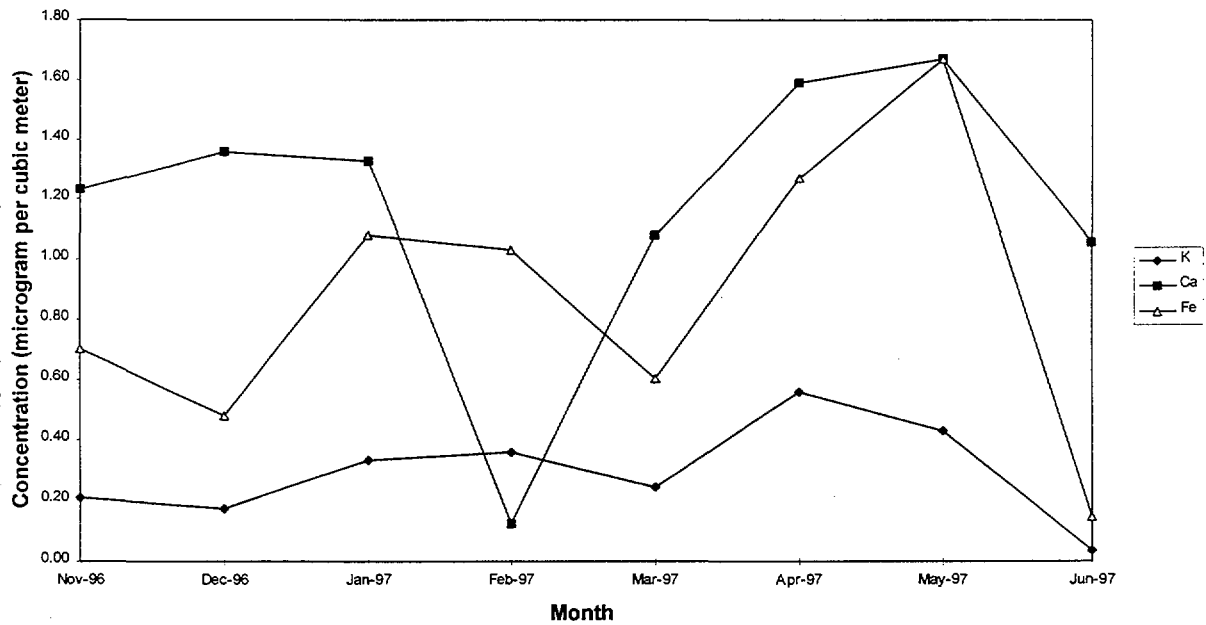Fig. 12 Variation of K, Ca and Fe for 0.4 μm Filter
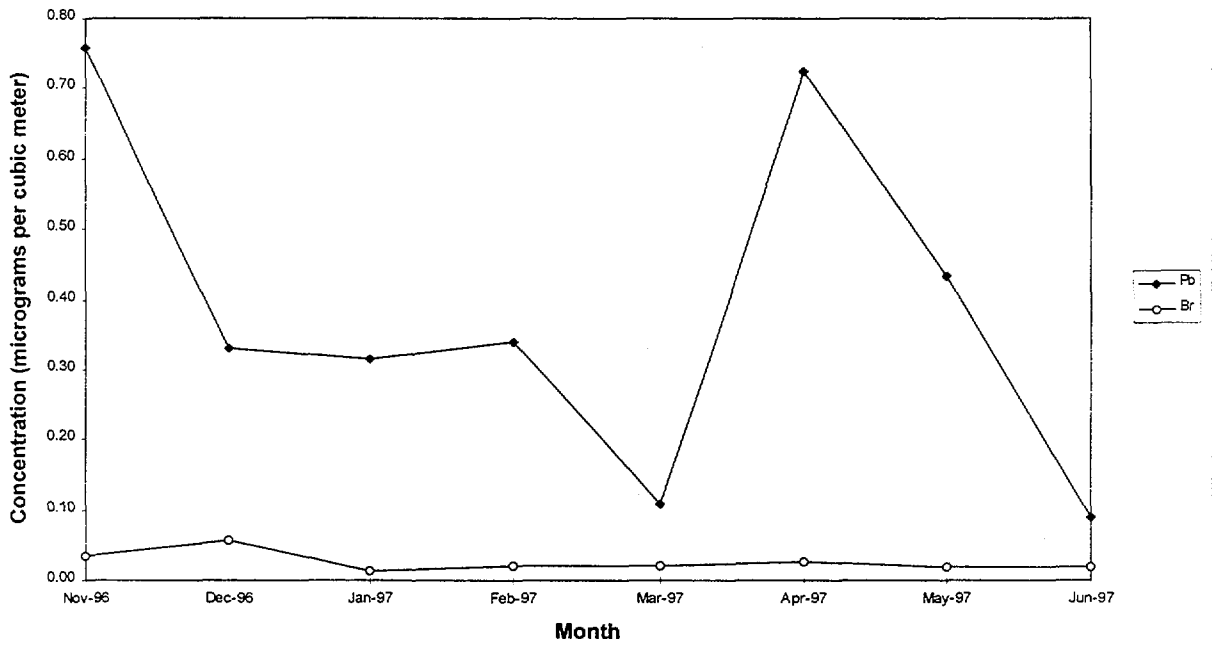
Fig. 13 Variation of Br and Pb for 8 μm Filter

Fig. 14 Variation of Br and Pb for 0.4 μm Filter