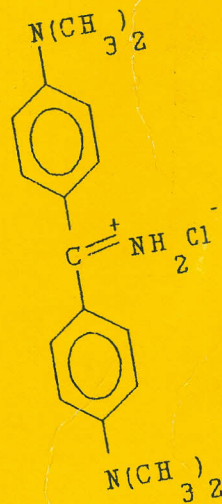
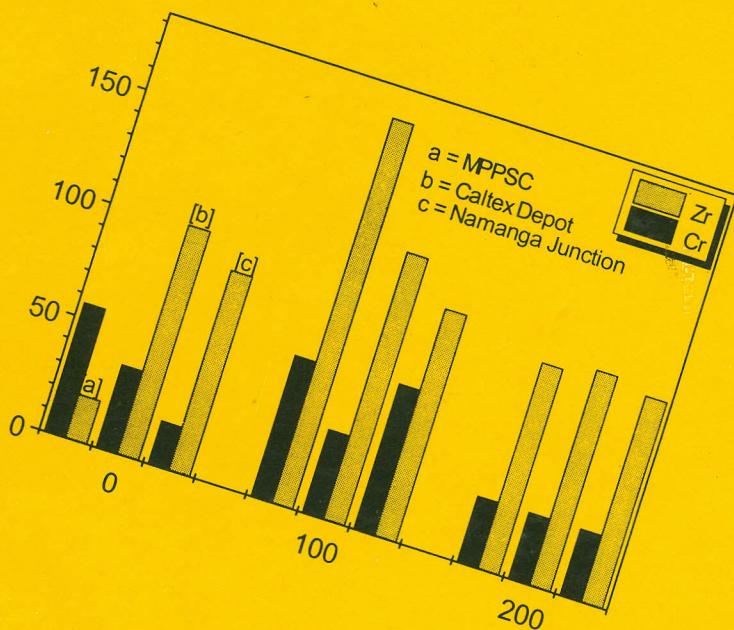


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$$T = \langle \chi_f(\mathbf{k}_f, \mathbf{r}_2) \varphi_f(\mathbf{r}_1) | \frac{1}{r_{12}} | \Psi_i^+(\mathbf{r}_1, \mathbf{r}_2) \rangle$$



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## Analysis of soil for trace elements along two highways of Kenya

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Energy dispersive X-ray fluorescence technique has been used to study the levels of lead and other toxic trace elements in the soil samples collected along two major highways (Mombasa and Thika) of Kenya at the various distances off the road. The soil samples from Thika road are found to have higher concentration values of the trace elements: Cr, Zr; Mn, Fe, Y; Ni, Cu, Zn, Br and Sr than those from Mombasa road. The samples from Thika and Mombasa roads have maximum concentrations of Lead, 56 µg/g and 90 µg/g respectively at the distance of 100m off the roads, which is below the admissible value of 250 µg /g for agricultural practices.

**Key words:** XRF analysis; pollution; trace elements; nuclear techniques; radiation; detection

### INTRODUCTION

For a long time, the toxicity of metals was considered as an occupational hazard. Industrialisation, urbanisation, increased vehicular traffic and use of fertilisers and pesticides in agriculture have resulted in increased contamination of environment by heavy metals. The toxicity of metals in the environment is becoming a matter of concern for the general population. It has been observed that the toxic metals, attributed to vehicular emissions, such as Lead, are deposited at relatively short distances from the road. Hay (1984) has reported that about 200,000 tons of lead is deposited on the earth annually due to the use of tetra-ethyl lead and tetra-methyl lead in fuel. Studies on the toxicity and essentiality of toxic trace elements have been carried out by several researchers (Nelson, 1991; Reichlnayr-Lais & Krichgebner, 1991; Mukhtar *et al.*, 1991; Duane *et al.*, 1996; Hong & Ha, 1996; Oluwole *et al.*, 1994; Ostachowicz *et al.*, 1995; Murti Krishna & Viswanathan, 1991; Heavy metal task force, 1991). At the same time, all mineral elements are essential to the environment, human beings and animals but their excess may lead to serious health hazards. Kinyua *et al.* (1991, 1993) have reported the concentrations of mercury, lead, cadmium, copper, manganese and iron in water and fish

samples from Nairobi-Athi river, and Naivasha area in Kenya, respectively. The study of the levels of mercury in water, fish, sediments and blood samples from different regions of Kenya have been done by Kamau *et al.* (1991).

The adjacent lands along most major highways of Kenya are left as open spaces, or used for small scale farming and grazing of cattle and livestock. Some grass and plants are expected to have high levels of lead and other toxic metals. So far, no study has been carried out to determine the concentrations of toxic metals in soil samples along Thika and Mombasa highways of Kenya. This work will be important and essential to study the impact of pollution on the health and environment.

### EXPERIMENTAL

#### a. Sampling and sample preparation

The soil samples for the trace element analysis were collected at about 10 km intervals along the road and at 100 m intervals off the road. On Thika road at (a) Kasarani (b) Kenya Clay Products (KCP) (c) Juja and on Mombasa road at (a) Mombasa Penny Profit Store centre (MPPSC) (b) Caltex depot (c) Namanga junction, sampling was done at the top layer (< 5 cm depth). Samples were collected in the clean plastic bags and stored at 4°C to retard the compositional changes due to biological

activity (Barbara Holynska, 1993). The soil samples collected were ground to fine particle size of less than 50µm after oven drying at 105° C for 48 hours. For each sample, at least three pellets weighing between 100–200mg/cm<sup>2</sup> were prepared for analysis.

### b. EDXRF system

The energy dispersive X-ray fluorescence analysis system consists of an X-ray spectrometer and a radioisotope excitation source. The radiation from the radioactive source, Cd<sup>109</sup> (half life, T<sub>1/2</sub> = 453 days and activity = 10mCi) are incident on the sample which emits the characteristic X-rays. These X-rays are detected by Si(Li) detector (EG&G Ortec, 30mm<sup>2</sup>x10mm sensitive volume, 25µm Be window) with a energy resolution of 200 eV at 5.9keV Mn K<sub>α</sub> - line. The spectral data for analysis were collected using personal computer based Canberra S-100 multichannel analyser (MCA). The acquisition time applied in the EDXRF measurements was 1000seconds.

### c. Data analysis

X-ray spectrum analysis and quantification was done using IAEA QXAS software (QXAS, 1992) which is based on the fundamental parameters method (FPM) (Sparks, 1975; Giauque *et al.*, 1973, 1977). For each pellet sample, three intensity measurements were taken: sample alone, sample with multi-element target and target alone accordingly for absorption matrix effect corrections using the Emission – Transmission Technique (Sparks, 1975; Giauque *et al.*, 1973, 1977). Consequently, elemental concentration values were calculated using the intensity equation developed for intermediate samples based on fundamental parameters method (FPM).

$$I_i(E_i) = G_0 K_i \varepsilon(E_i) \alpha_i \frac{(1 - \exp\{-a\rho d\})}{a\rho d} \quad (1)$$

Where:

$I_i(E_i)$  is the measured fluorescent intensity of element i:

$G_0 = I_0(E_0) \Omega_1 \Omega_2 \csc \phi_1$  is the geometrical constant:

$K_i$  is the relative excitation-detection efficiency for element i and is given by

$$K_i = \sigma_i^{\text{ph}}(E_0) \left(1 - \frac{1}{J_K}\right)^i f_k^i \omega_k^i, \quad (2)$$

$\sigma_i^{\text{ph}}(E_0)$  is the photoelectric cross section of an element i for the primary radiation of energy  $E_0$ :  
 $\omega_k^i$  is the fluorescence yield of an element i in the K-shell:

$f_k^i$  is the ratio of intensity of a given K or L line to the intensity of the whole series:

$\rho$  and  $d$  are the density and thickness of the sample:

$\varepsilon(E_i)$  is the relative efficiency of the detector at energy  $E_i$ :

$\alpha_i$  is the elemental concentration of element i in gm/cm<sup>2</sup>:

$a = \mu_0(E_0) \csc \phi_1 + \mu_1(E_i) \csc \phi_2$  is the total mass absorption coefficient for primary and fluorescent radiation in the sample.

$\phi_1$  and  $\phi_2$  are the angles formed by the directions of the primary and fluorescent radiation with the sample surface respectively.

For quality control of measurements, we have analysed certified reference materials: IAEA (Soil-7) by the same method. For most elements, the accuracy on concentration value is of the order in the range between 5 and 10% (Table 1). The lower limits of detection (LLD) values for solid samples prepared in the pellet forms were obtained from the analysis of IAEA soil-7 samples (Table 1). These values were calculated according to the following equation (Jenkins *et al.*, 1995):

$$\text{LLD} = \frac{3}{m} \sqrt{\left(\frac{R_b}{T_b}\right)}, \quad (3)$$

Where  $R_b$  is the background counting rate (c/s):

$T_b$  is the time for background counting rate:

$m$  is the sensitivity in c/s (µg/g)

## RESULTS AND DISCUSSION

The results for the analysis of soil samples along two major highways of Kenya are given in tables 2 and 3. The variations of the concentrations of lead and other trace elements: Mn, Fe, Y, Ni, Cu, Zn; and Cr, Zr with the distances of 0m, 100m, 200m off the roads are shown in figures [1-8]. The data show that the lead concentrations are found to be in the range (16-56) µg /g and (6-90) µg /g on Thika and Mombasa roads respectively. The higher values

of lead concentrations on Mombasa road may be due to heavy and more traffic on this road on compared to traffic on Thika road. The highest iron concentration of 237 mg /g is found at about 100m from Thika road near the Kenya Clay Products (KCP). This may be as a result of the accumulation of the clay dust from the manufacturing processes of the bricks and other clay products. The concentration values of Mn, Fe, Y; Ni, Cu, Zn; Cr, Zr at about 100m are generally higher in the samples from the Thika road than those from Mombasa road.

In this paper, the variation in the concentration values of the trace elements in the samples at the various distances off the roads is considered to be of more interest than the uncertainty in the concentration values. However, the achieved accuracy of the elemental determination was better than 10%, but as expected, was much worse (up to 20%)

for the trace elements whose concentrations were close to the detection limit.

## CONCLUSION

The mean lead concentration in the samples collected from Mombasa road especially at the Namanga junction has been found to be higher than those from Thika road. The highest lead concentration of 90 $\mu$ g/g, which is below the admissible value of 250 $\mu$ g/g for agricultural practices (Murti Krishna & Viswanathan, 1991; Heavy metal task force, 1991), was determined in the samples collected along Mombasa road. However, prolonged exposures to even small doses of lead can cause lead poisoning. The concentrations of other trace elements in the samples are also much below the trigger levels (Murti Krishna & Viswanathan, 1991; Heavy metal task force, 1991).

**Table 1.** Results of XRF analysis of a certified reference material-IAEA (Soil-7)  
(concentration values in  $\mu$ g/g , \*mg/g, N=5)

Element	Our values	Certified mean values	LLD values
K	12.4 $\pm$ 0.9*	12.1*	834
Ca	166 $\pm$ 11*	163*	414
Ti	2.9 $\pm$ 0.2*	3.0*	84
Cr	76.1 $\pm$ 18	60	25
Mn	584 $\pm$ 43	631	22
Fe	25.4 $\pm$ 1.6*	25.7*	20
Ni	—	—	9.6
Cu	30.2 $\pm$ 3.8	11.0	8.5
Zn	104 $\pm$ 7	104	8.3
Br	6.8 $\pm$ 0.7	7.0	2.3
Sr	105 $\pm$ 7	108	4.0
Y	20.1 $\pm$ 1.4	21.0	2.7
Zr	183 $\pm$ 11	185.0	3.2
Nb	6.5 $\pm$ 0.5	12.0	6.4
Pb	65.4 $\pm$ 6.0	60.0	18

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**Table 2. Elemental concentration values ( $\mu\text{g/g}$ , \*  $\text{mg/g}$ , N=3)**

Element	Thika road								
	Kasarani			K.C.P.			Juja		
	0m	100m	200m	0m	100m	200m	0m	100m	200m
Cr	210	104	76	429	856	162	563	382	497
Zr	265	423	431	661	842	658	702	1050	1140
Mn*	9	3	2	18	13	5	12	9	10
Fe*	227	81	137	106	237	36	148	98	22
Y*	1	2	2	0.04	60	108	0.03	73	80
Ni	9	5	5	19	77	7	24	18	27
Cu	25	23	17	17	33	19	21	18	29
Zn	19	14	10	111	127	90	25	22	29
Pb	16	26	21	46	55	22	56	44	49
Br	6	3	3	2	4	4	1	2	3
Sr	47	68	68	54	34	56	52	29	35

N= number of determinations.

**Table 3. Elemental concentration values ( $\mu\text{g/g}$ , \*  $\text{mg/g}$ , N=3)**

Element	Mombasa road									
	MPPSC			Caltex			Namanga junction			
	0m	100m	200m	0m	100m	200m	0m	100m	200m	
Cr		56	62	29	36	37	29	19	64	29
Zr	19	170	91	101	118	95	88	100	91	
Mn*	0.07	0.04	0.4	1	1.4	0.5	0.5	0.5	0.4	
Fe*	23	0.7	22	3	4	4	23	29	22	
Y*	0.7	0.004	0.6	0.7	0.7	0.6	0.7	0.7	0.4	
Ni	2	26	2	3	3	2.5	26	1	2	
Cu		1.3	1.5	2.5	2.4	2	3.5	5	9	3.5
Zn		2.4	3	3	5	3	4	10	3	4
Pb		67	7	10	42	58	56	70	90	51
Br	1	6	1.5	2	1	1.5	1	1.4	1.5	
Sr	51	3	28	35	22	28	30	27	28	

N= number of determinations.

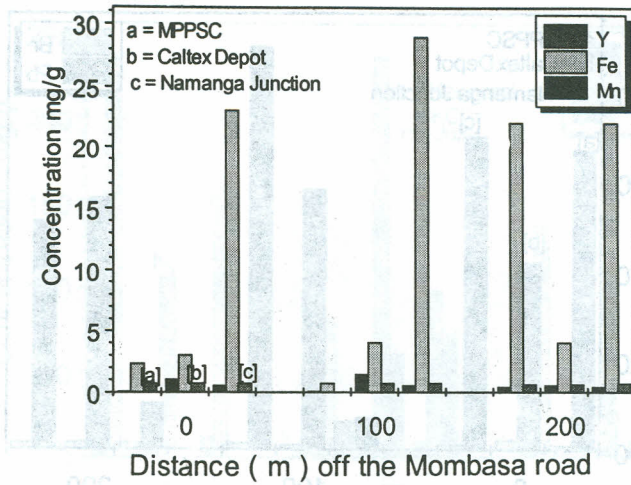


Figure 1. Levels of Mn, Fe, Y along Mombasa road.

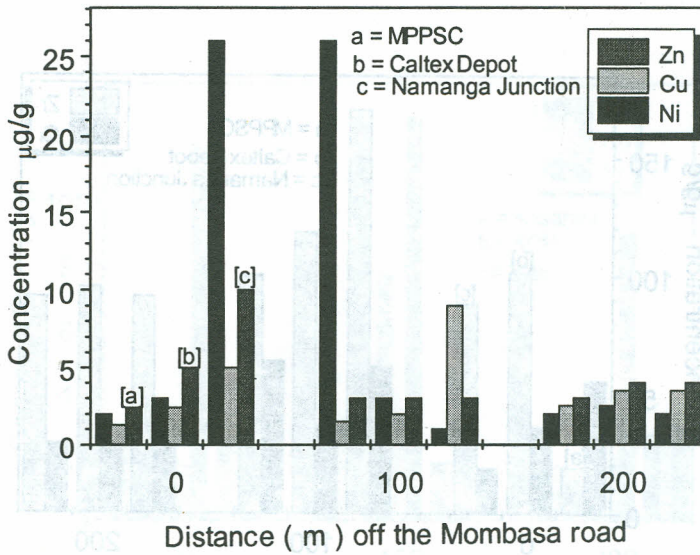


Figure 2. Levels of Ni, Cu, Zn along Mombasa road.

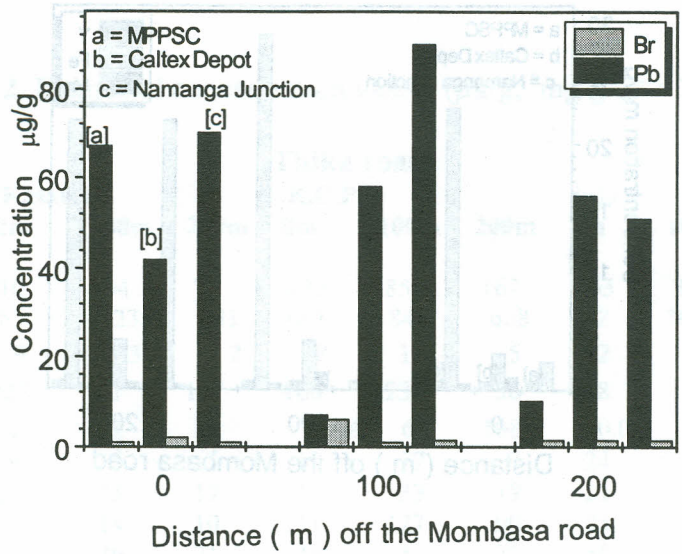


Figure 3. Levels of Pb and Br along Mombasa road

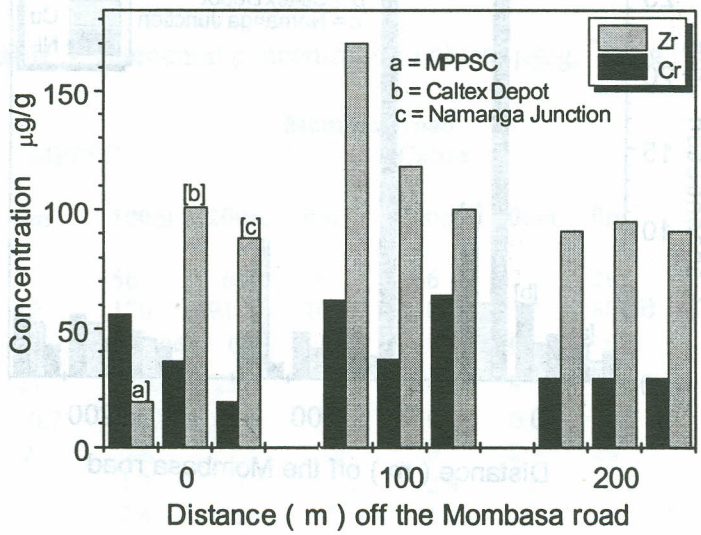


Figure 4. Levels of Cr and Zr along Mombasa road.

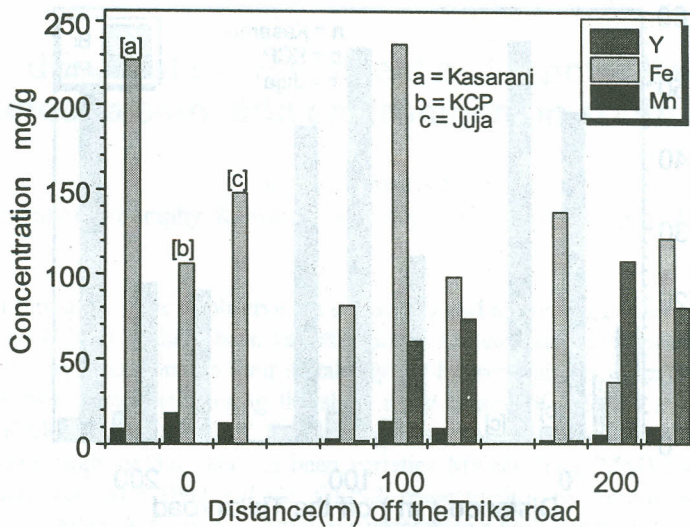


Figure 5. Levels of Mn, Fe, Y along Thika road.

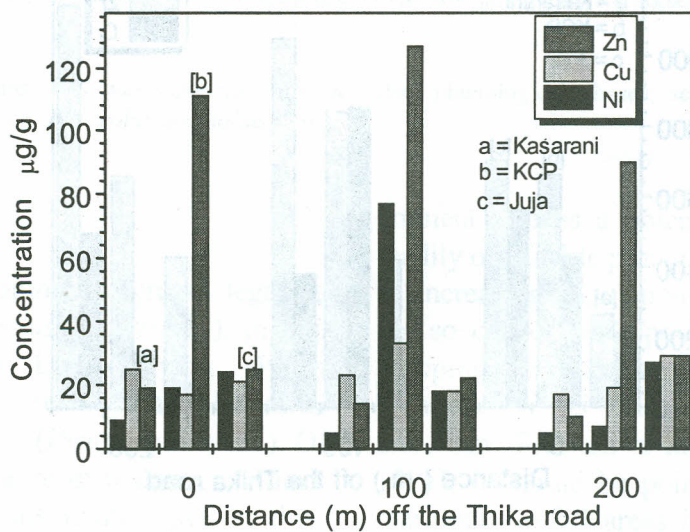


Figure 6. Levels of Ni, Cu, Zn along Thika road.

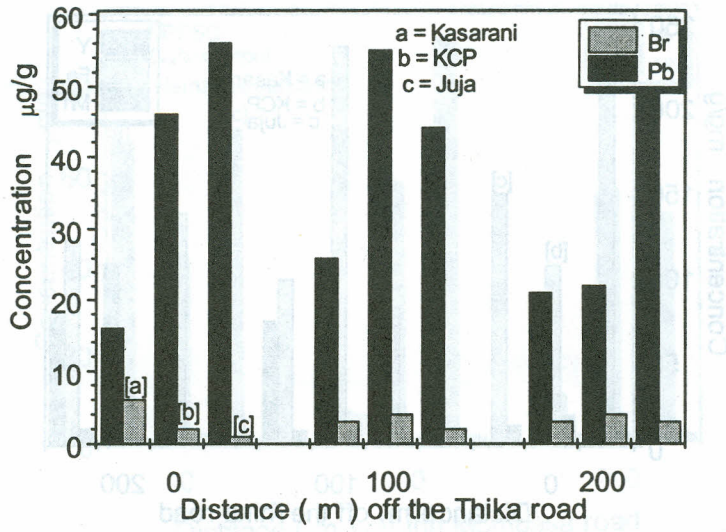


Figure 7. Levels of Pb and Br along Thika road.

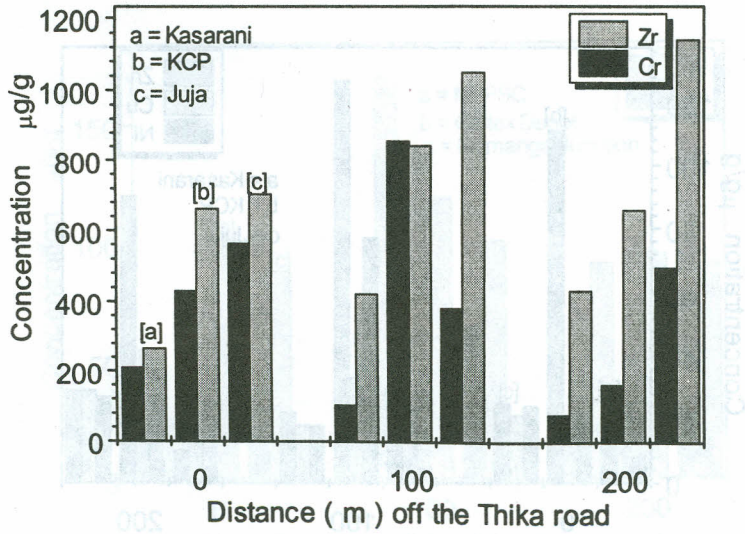


Figure 8. Levels of Cr and Zr along Thika road.