



Source identification of airborne elements in industrial area by XRF technique

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Abstract

In this work, X-ray fluorescence was applied to analyze aerosol samples collected from indoor and outdoor atmosphere Sudan Mint Company in Khartoum industrial area. The collected X-ray spectra were analyzed using AXIL program. The concentration of Calcium, Chromium, Iron, Cobalt, Nickel, Copper, Zinc, Bromine, and Lead were determined compared to the prepared standards. The accuracy of the results was crosschecked using Atomic Absorption Spectrometer. Various receptor models were used in aerosol source identification and apportionment. In this study, the Zinc and Copper showed highest concentration in the indoor and outdoor samples. The correlation between the elements showed that the elements were contributed by the same source. The principal factor and enrichment factor confirms the elements in industrial area aerosol are industrial emission and soil dispersion. The data can be used by occupational health department to assist in drafting policies on work places to control pollutants.

Keywords: Aerosol, pollution, industrial, atmosphere, metal, Sudan

Introduction

Monitoring the heavy metal pollution is an important task in air quality assessment. The major source for these heavy metals is industrial emission. Increased supply of these pollutants to air leads to natural trace metal imbalance and environmental degeneration. Pollution levels in the environment may lead to poor health and decreased life expectancy. Most harmful effects in the environment arise from exposure to urban industrial pollutants. The heavy metals are toxic if ingested or inhaled at sufficiently high levels for long enough periods (Jones, 1999).

Soil dust is common components in air, and it contributes to the measured values of Si, K, Ca, Fe, Zn, Br and Pb. Emission from industrial sources depends on the type of the process involved, the quantity of petroleum products employed and the types of fuel and raw materials used.

Enrichment factor was calculated to differentiate between the elements that originate from anthropogenic emission and that of crustal origin. The enrichment factor is usually calculated through the equation.

$$EF(x) = \frac{\left(\frac{x}{Ref}\right)_{aerosol}}{\left(\frac{x}{Ref}\right)_{source}}$$

where $EF(x)$ = the ratio of element to reference material. The reference material used in this calculation is the composition of crustal rock. In this study Fe is used as reference element (Philip K. Hopke *et al.*, 1976).

In factor analysis, the factors are derived from the matrix of linear correlation coefficients taken pair-wise

over all the variables (Kristian Keiding *et al.*, 1986). The factor analysis tried to maximally reproduce this matrix. The reproduced correlation coefficient is calculated from the common factor coefficient. The factors are considered to be those fundamental parameters that govern the values of the observed data. In factor analysis, the variance is apportioned between the common factors and the unique factor. The objectives of factor analysis are then to identify the true dimensionality of the problem, the measures of interrelation between the variables, and the importance of each of these actual causal factors to the observed parameter value for each sample. This can be achieved by observing the correlation between each pair of vectors. The correlation between any two unit-length vectors is the cosine of the angle between them. The matrix is calculated according to

$$X_{ij} = \frac{x_{ij} - m_j}{S_j}$$

Where m_j = the mean of the original entries of the i th vector S_j = the standard deviation of the original entries of the i th vector (George T. Wolff *et al.*, 1986; Eugene Kima *et al.*, 2003).

Varimax rotation perturbs the eigenvectors to maximize the variance within each vector. As a result for each vector, the number of variables with intermediate loading is decreased, and the number with either very large or very small loading is increased. In other words, the rich get richer and the poor get poorer. The numbers of significant eigenvectors is determined by an appropriate means and the error is discarded.

Materials and methods

In order to evaluate the environmental impact of particular pollutants and to devise a plan for improving the

atmospheric environment, it is important to grasp accurately the relation between the emission intensity from pollutant sources and the concentration at receptors. This calls for the utilization of highly sensitive methods of analysis. The X-ray emission technique is the one of choice in assessing the amount of the environmental pollution (Mier & Unger, 1976).

Table 1. Sensitivity of some elements

Compound	Element	E(KeV)	a(E1,Ei)	apd	T	I	Si
NaCl	Cl17	2.622	532.1	218.7	0.005	1.562	1370
K2SO4	K19	3.31	213.2	94.24	0.010	6.726	3562
CaCO3	Ca20	3.69	131.1	52.48	0.190	20.31	6652
K2CrO4	Cr24	5.412	219.2	96.88	0.010	25.93	21282
FeO3	Fe26	6.399	92.37	38.19	0.261	452.5	59758
Co	Co27	*	*	*	*	*	79229
Ni	Ni28	*	*	*	*	*	96891
Cu2SO4	Cu29	8.048	56.79	23.99	0.041	482.7	112743
ZnSO4	Zn30	8.639	52.26	21.89	0.045	1059.5	130405
KBr	Br35	11.924	68.67	28.06	0.035	3362.9	358324
SrCO3	Sr38	14.165	47.08	19.22	0.052	3433.9	445859
ZrOCl	Zr40	15.775	88.07	36.91	0.027	3660.1	504261

Where a = absorption coefficient, ρ = density (g/cm^3), d = sample thickness cm,

T = absorption factor, I = intensity, Si = sensitivity

Atmospheric aerosols were collected indoor and outdoor in industrial area in Khartoum lies in Sudan (15.58 latitude and 32.52 longitudes). Tuti Island was selected as a control area at the same location. The reason for that it is surrounded by Nile and farms, so it is least affected by industrial emission. Aerosol samples were collected on Nuclepore filters with diameter of 47 mm and pore size of $0.47 \mu\text{m}$ and thickness of $10 \mu\text{m}$, which is fabricated from polycarbonate, are used for sampling. Flow rates were measured at the beginning and end of each run by mean of flow meter. The sampling time ranged between one to two hours, but in some locations samples were collected for a period of three hours and for four hours in the control area. Thin standard for spectrometer calibration were prepared from standard solution for each element using two types of pre-concentrations physical and chemical pre-concentration. In this work, Ammonium Pyrrolidine Dithiocarbamate (APDC) was used as a co-precipitating agent. For each element of interest number of thin standards was prepared by using different concentration of element compound in chemical powders was used to prepared stock standard solution.

Direct analysis of filtered air

and standard is almost invariably done on a thin Nuclepore in a non-evacuated XRF setup. XRF emission spectroscopy is applied to elemental analysis of air particulate in sample by using radioactive source Cd^{109} . In energy dispersive mode, a Si(Li) detector used has an energy resolution of 180 eV, at $E_{k\alpha}$ (5.8 KeV) connected to a Canberra 35 plus (MCA) system is employed for acquiring the X-ray spectra.

One of the most important parameters, by which the performance of a spectrometer can be judged, is the sensitivity (Mier & Unger, 1976). Thick standards were prepared in pellet form from chemical compounds of known stiochemistry and these were used for sensitivity calculation. The calibration of Si (Li) detector is carried out by measuring the intensity of the thick standard to obtain for each element the sensitivity constant. The values of the sensitivity for the missing elements in X-ray range of interest are calculated using extrapolation, and the results are presented in Table 1.

Results and discussion

Functional relation of plotting concentration as independent variable and intensities as dependent variables gave linear relation of the data. The slope, intercepts and regression were used to calculate the elements concentration in aerosol samples of control area and indoor and outdoor of Sudan Mint Company in industrial area. After calibration of XRF spectrometer system by using the detector sensitivity method, the accuracy of the results was cross-checked by Atomic Absorption Spectrometer. The analytical results by XRF are agreed fairly well with atomic absorption results technique (AAS).

Concentrations were obtained after calibration of the X-ray intensity against standard concentration by using a series of fitting and correction methods. There is no need to apply any matrix correction calculation afterward. The intensity is linearly related to concentration of the element within the range studied (Mier & Unger, 1976). These calibration curve were then used in the concentration assignments for unknown element concentration in air samples. Fig.1 shows elements concentration of control site. The control site is showed the lowest elemental contamination as compared to the site under investigation, which includes that the major source in the control cite atmosphere for these element is soil dispersion.

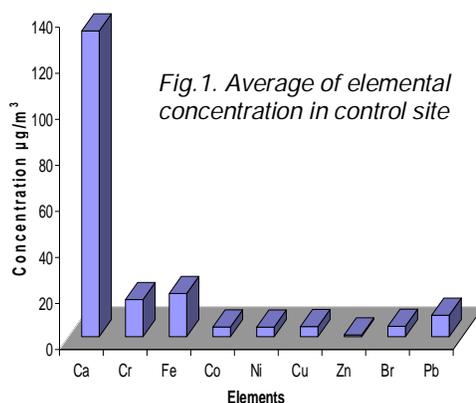


Fig.2. Average of elemental concentration in Sudan Mint Company indoor site

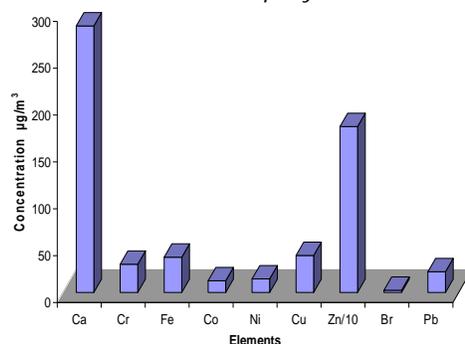


Table 2. Correlation between elemental concentrations of the Indoor

Element	Ca	Cr	Fe	Co	Ni	Cu	Zn	Br	Pb
Ca	1								
Cr	-0.12	1							
Fe	0.64	-0.03	1						
Co	0.74	0.15	0.97	1					
Ni	-0.52	0.82	-0.59	-0.44	1				
Cu	-0.89	-0.18	-0.86	-0.94	0.38	1			
Zn	-0.86	-0.01	-0.94	-0.97	0.55	0.97	1		
Br	0.80	0.36	0.22	0.42	0.08	-0.69	-0.53	1	
Pb	0.72	0.58	0.37	0.57	0.2	-0.77	-0.61	0.95	1

The Fig.2 displays graphically the elemental concentration of aerosol in Sudan Mint Company indoor area. Comparison of the mean values in Sudan Mint Company aerosol with control site shows high concentration for Cu, Cr, Fe, Co, Ni, Br, Zn and Pb.

Table 2 shows correlation between elemental concentration data from Sudan Mint Company aerosol. The correlation between elements in this site confirms there are two sources of elements in this area. One source of these elements is foundry, which uses Cu, Zn, Fe, for casting coins, and oil burning for melting raw material for these products. Other source may be soil dispersion source.

Aerosol elemental concentration of the Sudan Mint Company outdoor is plotted in Fig.3. The average aerosol elemental concentration of the outdoor site when compared to same data from control area revealed highest concentration from Ca, Cr, Fe, Co, Ni, Cu, Br and Pb.

The correlation of the elements in industrial area aerosol is included in Table 3. Ca, Cr and Fe are correlated with each other. Fe is correlated with Ni, Zn, Br. Co is correlated with Cu and Ni. Ni is correlated with Fe and Zn. These confirm that there are several sources of emission for elements in this area.

Enrichment factors were calculated using the overall mean concentration of the various elements. These calculations were done relative to the earth's crustal composition (Mason, 1966) and with Fe as the reference element. The results are given in Table 4 . These low enrichment factors are explained by the large amounts of soil dust and the relatively low industrial activity. Most of the element shows an enrichment factor close to unity indicating a soil dispersion source. It is seen from the Table 4 that Ca has low enrichment; the primary source for these elements is evidently soil. The elements, which are significantly enrichment in Sudan Mint Company

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Fig.3. Average of elemental concentration in Sudan Mint Company outdoor site in industrial area

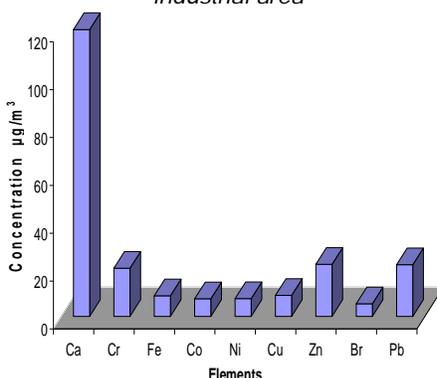
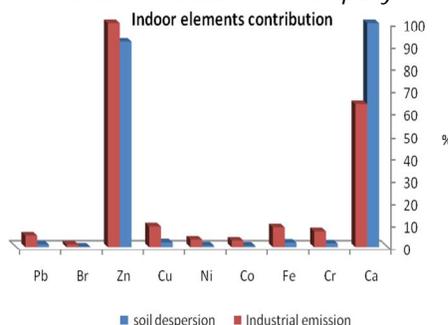


Fig.4. Shows element contribution in the indoor of Sudan Mint company



aerosol, are Zn, Cr, Cu, Fe, Br and Pb. All other elements shows an intermediate to high enrichment and are from anthropogenic emission with the possible exception of Zn and Cu in the indoor and outdoor, hence there will be significant contribution from foundry for these two elements.

The Variamx rotated principal Factor for indoor and outdoor aerosol data is presented in Table 5. The variance percentage associated with each factor is also included. The data of principal factor in table.5 shows high loading of Cr, Ni, Cu, and Zn in Factor 2, these indicate that the element are related to the anthropogenic emission (Philip K. Hopke *et al.*, 1976). Most of these elements are at least partially produced by anthropogenic emission activities and they are related to various combustion process.

Principal factor shows at factor 1 high loading of Cu in Table 5 (George T. Wolff *et al.*,1986). The factors and statistical data above suggest that the Pb, Fe, Br, and Ca probably due to combustion source or oil burn and coal burning, (Windester & Nifog,1971) have presented the elements tracer content of various types of fuel oil burning emission.

From all these relationships the low loading of element Ca, Cr, Fe and Co in Factor 1 in table.5 are partially indicate a soil dispersion source possible explanation for this is that the concentration of the crustal elements in the fine mode is more affected re-suspension of dust from within the city, e.g by traffic (Orsini *et al.*, 1982; Rita Van Dingenen *et al.*, 2004).

The results of data assessment shows in Fig.4 indicate the main contributions of the indoor elements are affected by soil desperation and industrial emission. In addition, the elements affect indoor are extended to outdoor and the same elements shown in industrial area

Table 3. Correlation between elemental concentration of the outdoor

Element	Ca	Cr	Fe	Co	Ni	Cu	Zn	Br	Pb
Ca	1								
Cr	-0.51	1							
Fe	-0.52	0.12	1						
Co	-0.69	0.59	-0.25	1					
Ni	-0.31	-0.36	0.88	-0.45	1				
Cu	-0.64	0.82	-0.20	0.94	-0.53	1			
Zn	-0.20	-0.66	0.60	-0.39	0.90	-0.59	1		
Br	-0.30	-0.38	0.87	-0.44	1.00	-0.53	0.91	1	
Pb	0.68	0.29	-0.49	-0.24	-0.66	0.00	-0.80	-0.69	1

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Table 4. Principal factor

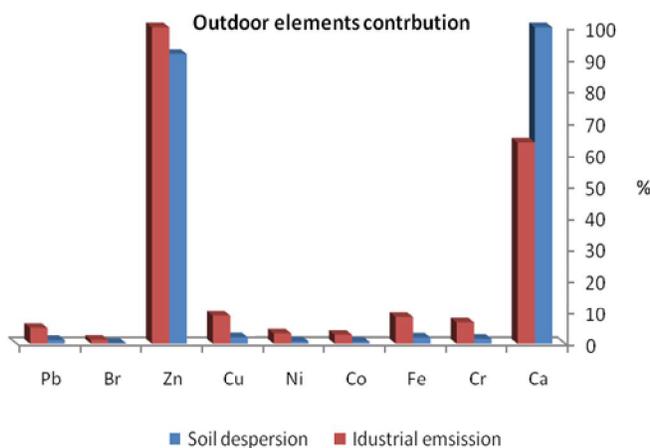
Elements	Factor 1	Factor 2	R ²
Ca	0.05	0.511	0.79
Cr	0.16	0.850	0.85
Fe	0.12	0.120	0.63
Co	0.25	0.270	0.41
Ni	0.57	0.750	0.74
Cu	0.82	0.850	0.84
Zn	0.51	0.730	0.79
Br	0.01	0.070	0.42
Pb	0.001	0.370	0.50
Total variance	32.9%	23.21%	

Communalities= R²; Rotation: Varimax normalized

Table 5. Enrichment factor for control, indoor and outdoor of SMC sites

Element	Control site	Indoor	Outdoor
Ca	9.75	10.4	19.23
Cr	430.44	399.1	1169.77
Fe	0	0	0
Co	453.09	663.13	1709.3
Ni	147.48	256.83	574.42
Cu	214.19	952.92	928.12
Zn	30.08	33578.2	1804.8
Br	4801.7	2809.5	12232.5
Pb	1912.83	2261.9	9660.11

Fig.5. Shows elements contribution in the industrial area



contributed from industrial emission and soil dispersion in Fig.5 (Paulo *et al.*,1988; Rita Van Dingenen *et al.*, 2004).

Conclusion

The analysis of aerosol samples in control area (Tuti Island) showed that the concentration of the elements studied is much lower than that of the industrial area. The indoor aerosol metal content of Tuti Island reflects the contribution of outdoor atmospheric pollution from the industrial site. Metals such as Zinc and Cu were recorded highest in the aerosols of industrial area. The data sites were subjected to principal factor analysis and enrichment factor calculation. The principal factor and

enrichment factor was useful with respect to source identification. This data showed that the aerosol of industrial area (indoor and outdoor of Sudan Mint Company) is affected by industrial emission and soil dispersion source. This research project provides base line data on urban air quality. The data is of value for the Ministry of Environment and Urban Planning.

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