Chemical Partitioning and Speciation of Some Trace Elements in Soil and Street Dust

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Chemical fraction technique and atomic absorption spectrometry (AAS) were used to determine the presence of Cr, Mn, Fe, Cu, Zn, Pb in surface soil samples and street dust collected from areas exposed to industrial and traffic emission and agricultural areas in Khartoum state, Sudan. Principle component analysis was carried out as an statistical method.

Key Words: Chemical partitioning, Trace elements, Soil and street dust.

INTRODUCTION

Elements present in natural materials at concentrations of < 1000 mg kg^{-1} have been defined as trace elements. Although some trace elements are essential to life, but many are toxic in high concentrations and transfer to food chain from soil to plant and then to the animal and so on[1]. But when this concentrations increase it become toxic and be hazardous for the health of and the balance of the environment it self, so the knowledge of the concentration of this pollutants is important.

Transferring of this pollutants to man, animal or plant depend on their chemical form, that means the knowledge of their total concentration, so it is important to know the chemical form of these metals. The environmental harmful effects of pollutant elements arise from urban industrial and agricultural pollutants. Although some of these effects are associated with traditional industrial processes, most are of fairly recent origin[2].

Sequential extraction is recognized as a useful methodology for gaining information on the origin, manner of occurrence, bio-availability, mobilization and transport of trace elements[3].

Study of trace elements content as a function of chemical speciation in soil and street dust from the study area was carried out. The hazardous effect of these trace elements on the environment is based on pH increase towards the neutral pH.

The purpose of the principle component method is to represent the variation present in the data without losing significant information. The dimensionality is reduced. To achieve this, new variables are constructed, according to a linear combination of the original variables in such a way that, the newly formed principle components are un-correlated, *i.e.* orthogonal in the *n*-dimensional space, where *n* is the number of the principle components.
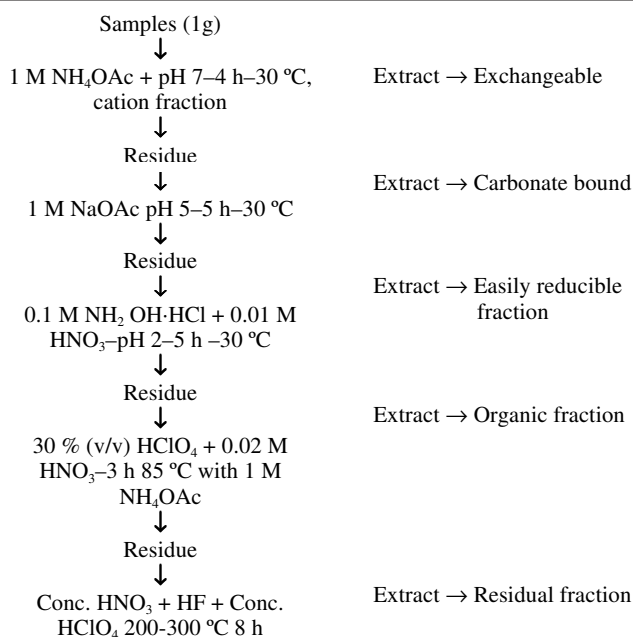
The principle components are constructed with decreasing degree of importance, *i.e.* the first principle represents as much variation as possible, the second represents as much variation as possible after variation explained by the first component have been removed, *etc.*[4].

EXPERIMENTAL

34 Samples of surface soil and street dust were collected (depth 0.5 cm) using plastic spatula and plastic jars, from Khartoum, Sudan. The locations were chosen carefully so as to provide good coverage of the densely industrial and traffic areas as follows: tanneries, printing presses, foundries, industrial areas, bridges entrances, traffic stations. Another group of samples from agricultural areas and free traffic streets were collected to serve as control. The samples were sieved using plastic sieve (0.2 mm) 1 g of sample was chemically fractionated as follows[5,6].

Fraction samples were analyzed using flame atomic absorption spectrophotometer (Perkin Elmer model 1130).

For the choice of reagents for sequential extraction particular emphasis was focused on the potential selectivity of each leaching solution. Many reagents including ammonium acetate[7], sodium acetate[8] and magnesium chloride[9] have been employed to liberate exchangeable metals. Of these, NH$_4$OAc (pH 7.0) has been the most extensively used in soil and sediment analysis. Reagents recommended for dissolving selectively the carbonate fraction in sediments, generally make use of sodium

Samples (1g)
↓
1 M NH₄OAc + pH 7–4 h–30 ℃,　　　Extract → Exchangeable
cation fraction
↓
Residue
↓　　　　　　　　　　　　　Extract → Carbonate bound
1 M NaOAc pH 5–5 h–30 ℃
↓
Residue
↓
↓　　　　　　　　　　　　　Extract → Easily reducible
0.1 M NH₂ OH·HCl + 0.01 M　　　　　　　　fraction
HNO₃–pH 2–5 h –30 ℃
↓
Residue
↓　　　　　　　　　　　　　Extract → Organic fraction
30 % (v/v) HClO₄ + 0.02 M
HNO₃–3 h 85 ℃ with 1 M
NH₄OAc
↓
Residue
↓
Conc. HNO₃ + HF + Conc.　　　　Extract → Residual fraction
HClO₄ 200-300 ℃ 8 h

acetate and/or acetic acid at acidic pH values[10]. Grossman and Millet[11] reported that organic carbon and free ion concentrations in noncalcareous soil samples were unchanged after contact with this buffer for 9 weeks. Other workers[9,12] have demonstrated that lower pH values lead to partial attack of Fe and Mn oxides. The most successful methods for leaching iron and manganese oxides involve the combined action of reagents reducing these metals to their ferrous and manganese forms respectively and of agents capable of keeping them in solution. The relatively large amounts of metals liberated, the two pairs most often used are hydroxide-acetic acid[9,13] and sodium dithionite-citrate pairs[9,14], Anderson and Jenne[15] found that trace metal concentration were consistently lower in leaching obtained with dithionite-citrate than in those obtained with hydroxylamine hydrochloride-acetic acid. Furthermore, several additional problems are raised by the utilization of the dithionite-citrate pairs: (1) Dithionite is highly contaminated with zinc and its purification by chelation-extraction procedure proves very difficult[16]; (2) They observe frequent collagen of the burner upon the analysis of the aqueous extracts by flame AAS. Hydrogen peroxide in acidic media is generally used to oxidize organic matter in soil and sediment[14] analysis, even though oxidation of all forms of organic matters may not be complete[8]. More efficient methods for destroying organic matter do exist (*e.g.* concentrated nitric acid used separately or in combination with hydrochloric acid or perchloric acid). Procedure for dissolving primary and secondary minerals (residual fraction) usually involve either alkaline fusion[9] or dissolution with mixers of hydrofluoric acid[16] and some other strong acids, (*e.g.*, nitric acid or perchloric acid).

The components that were extracted from the data are rotated in such a way that the variables are highly correlated with one factor or others. Here, VARIMAX rotation (a type of orthogonal relation that is widely used) was selected.

RESULTS AND DISCUSSION

Quality control of the obtained data was performed through the analysis of the certified reference material (CRM)

of soil-5. Table-1 shows the analytical and the certified values, the percentage error and recovery for the studied elements with the respect to the certified reference material. From this table one can conclude that there is good agreement between certified and analytical values, which indicates good percentage error and good recovery for metals under study. Table-2 (a-f) shows summary statistics for the concentration of the trace elements in each separated fraction and the total fraction using atomic absorption spectrometer. Table-2g shows the sum of the concentration for the five fractions From tables it is observed that the total concentrations of the trace elements in the bulk samples are in agreement quite well with the sum of the concentration of the elements in the five fractions. This serves as a means of verification of the results. There is a high standard deviation for all elements in all fractions except manganese in the bulk samples. Manganese and iron in the organic fraction and residual fraction and manganese in the other fractions high standard deviations result from wide variation of the elemental content in soil and street dust from the study area and *vice versa* for low standard deviation. The median for all elements-except manganese-in all fractions is not similar to the average, which means that there is a variation of the elemental contents. From these tables, one can conclude that the elemental content in soil and street dust under study is highly scattered and there could be an anthropogenic sources of these elements.

TABLE-1
COMPARISON OF THE AAS RESULTS OBTAINED IN THIS WORK WITH THE CERTIFIED VALUES FOR THE CRM OF SOIL-5

Element	Certified value	Analytical value	Error (%)	Recovery (%)
Cr (mg/kg)	29	30.0	3.4	103
Mn (mg/kg)	850	840	1.1	98.8
Fe (%)	45	40.6	9.0	90.2
Cu (mg/kg)	77	100	29	129.9
Zn (mg/kg)	368	300	18	81.5
Pb (mg/kg)	130	126	3.0	97.0

CRM = Certified reference material

TABLE-2a
STATISTICS FOR THE TRACE ELEMENTS CONCENTRATION (μg/g) EXCEPT Fe mg/g FOR THE EXCHANGEABLE FRACTION USING AAS

Summary of statistics	Element					
	Cr	Mn	Fe	Cu	Zn	Pb
Average	1.3	25.3	0.98	25.8	8.5	91.8
SD	3.7	16.6	1.27	121.4	17.7	421.9
Median	1.9	25.6	1.13	51.0	11.7	177.1
Min	*	4.4	0.02	0.03	0.01	–
Max	15.7	67.5	4.9	720.3	80.4	2500

TABLE-2b
STATISTICS FOR THE TRACE ELEMENTS CONCENTRATION (μg/g) EXCEPT; Fe mg/g FOR THE CARBONATE CATION FRACTION USING AAS

Summary of statistics	Element					
	Cr	Mn	Fe	Cu	Zn	Pb
Average	0.3	23.3	5.50	42.7	14.3	60.0
SD	1.2	17.5	15.4	197.8	30.7	257.2
Median	*	19.0	1.50	1.80	0.90	7.80
Min	*	1.20	0.30	0.05	0.01	0.50
Max	5.8	67.0	91.7	1174	110	1534

TABLE-2c
STATISTICS FOR THE TRACE ELEMENTS CONCENTRATION
(µg/g) EXCEPT; Fe mg/g FOR THE Fe-Mn OXIDES
FRACTION USING AAS

Summary of statistics	Element					
	Cr	Mn	Fe	Cu	Zn	Pb
Average	1.4	20.0	13.2	51.4	6.20	79.7
SD	4.4	11.1	15.3	199	13.9	274.8
Median	*	20.1	10.0	4.40	0.80	12.8
Min	*	1.20	1.30	0.20	0.01	1.20
Max	18.3	47.0	88.4	1158	60.1	1624

TABLE-2d
STATISTICS FOR THE TRACE ELEMENTS
CONCENTRATION (µg/g) EXCEPT; Fe mg/g FOR
THE ORGANIC BOUND FRACTION USING AAS

Summary of statistics	Element					
	Cr	Mn	Fe	Cu	Zn	Pb
Average	32.6	22.5	26.1	17.1	11.0	55.5
SD	60.8	19.3	17.1	28.0	31.0	143
Median	3.10	16.8	20.4	6.80	1.30	9.70
Min	*	1.40	3.00	0.10	0.01	0.40
Max	220.5	86.0	91.4	113.3	150.7	832

TABLE-2e
STATISTICS FOR THE TRACE ELEMENTS
CONCENTRATION (µg/g) EXCEPT; mg/g FOR
THE RESIDUAL FRACTION USING AAS

Summary of statistics	Element					
	Cr	Mn	Fe	Cu	Zn	Pb
Average	16.7	23.3	27.5	8.00	3.20	21.0
SD	38.8	11.3	15.1	16.8	5.00	61.7
Median	10.5	21.0	23.0	3.00	0.10	5.60
Min	*	2.90	7.00	0.05	0.01	0.90
Max	235.5	50.6	90.2	90.4	23.7	365

*under detection limit

TABLE-2f
STATISTICS FOR THE TRACE ELEMENTS
CONCENTRATION (µg/g) EXCEPT; mg/g FOR
THE BULK SAMPLES USING AAS

Summary of statistics	Element					
	Cr	Mn	Fe	Cu	Zn	Pb
Average	53.1	114.5	93	119	66.5	301
SD	78.1	48.3	91	398	71.9	1062
Median	16.6	107.5	7.03	20.3	40	74.3
Min	0.7	20.0	2.05	0.5	4.5	9.5
Max	315	250	46	2305	280	6200

TABLE-2g
SUMMATIONS OF THE AVERAGE FOR TRACE ELEMENTS
CONCENTRATION (µg /g) EXCEPT; Fe mg/g FOR THE FIVE
FRACTIONS SAMPLES USING AAS

Summations of element Concentration	Element					
	Cr	Mn	Fe	Cu	Zn	Pb
	52.3	114.4	73.28	127.6	43.2	308

Fig. 1(a-f) show the distribution of some trace elements in Khartoum's soil and street dust in different chemical fractions. From the figures the following observations can be conducted: for chromium (Fig. 1a), the highest concentration appears in the 4th fraction (organic fraction) with pH 2 so the bio availability of Cr is not easy. The concentration of Cr in those samples is higher than for control samples this mean that most

of the chromium in the soil and street dust under study have an anthropogenic source.
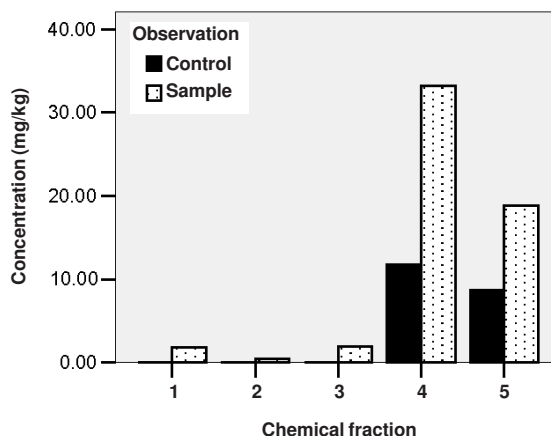

Fig. 1a. Distribution of Cr in Khartoum soil and street dust in chemical fractions

For manganese (Fig. 1b), the concentration of this element distributes through all the fractions without big differences in concentration. It is also observed that the concentration of control samples is higher than the concentration of samples except in exchangeable fraction and little bit in residual fraction where the concentration of samples is higher than for control samples, this give an indication that most of Mn in this study have natural sources.
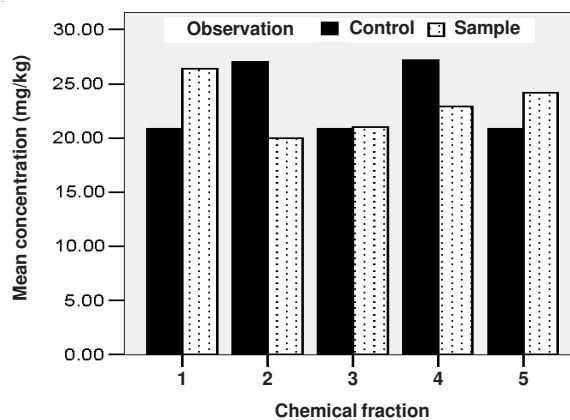

Fig. 1b. Distribution of Mn in Khartoum soil and street dust in chemical fractions

For iron (Fig. 1c), the high concentration of this element appear in fraction 4 as well as fraction 5 indicating that the bioavailability of this elements is hard. The ion concentration of the control samples is also high, which means that major fraction of this element in the samples under study come from natural source. For copper, zinc and lead the higher concentrations of these elements are in 3rd fraction (Fe-Mn oxide fraction), 2nd fraction (carbonate fraction) and 1st fraction (exchangeable fraction) respectively, thus their bioavailability order : Pb > Zn > Cu. Also the concentrations of these elements in samples are higher than the concentrations of those in control samples. This gives an indication that these elements have anthropogenic source.
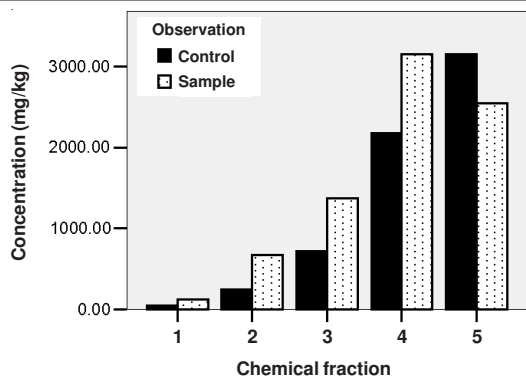
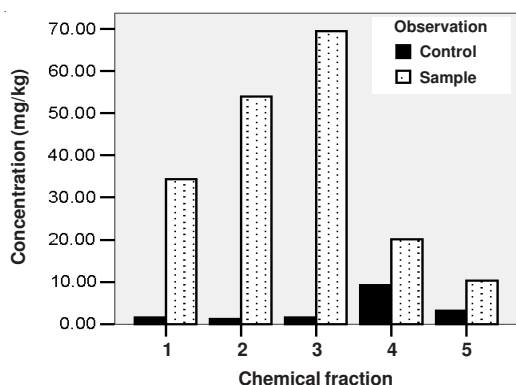Fig. 1c. Distribution of Fe in Khartoum soil and street dust in chemical fractions

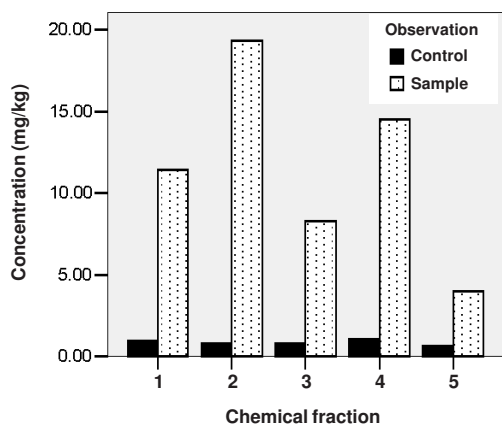Fig. 1d. Distribution of Cu in Khartoum soil and street dust in chemical fractions

Fig. 1e. Distribution of Zn in Khartoum soil and street dust in chemical fractions
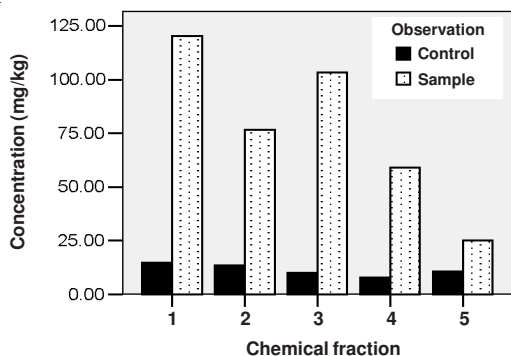

Fig. 1f. Distribution of Pb in Khartoum soil and street dust in chemical fractions

The comparison of these results with available global data as follows: Fergusson *et al.*[17] listed the percentage of Pb, Zn,Cu, Mn and Fe in street and house dust in different chemical fractions. Fergusson and Ryan[18] have also reported the distribution of the elements in the chemical fractions as shows in Table-3a. Harison *et al.*[19] found the distribution of the elements as shown in Table-3b. Gibson and Farmer[20] have listed the distribution of the elements in chemical fractions as shown in Table-3c. The results of the measurements of the concentrations of those trace elements in our study area have shown that the percentage of chromium is (61, 31 %) in both the organic and residual fractions respectively. The distribution of manganese is a proximately the same in all fractions, but Fergusson *et al.*[17] have shown that a good proportion of Mn is extracted from the Fe-Mn oxide fraction and the rest remain in the residual fraction. It was also noticed that 51 % of Mn extracted from residual fraction[18]. The percentage of iron is Fe (53, 37 %) in the organic and residual fractions respectively. Fergusson *et al.*[17] have obtained 87% of Fe extraction from residual fraction.

TABLE-3a
DISTRIBUTION OF SOME TRACE ELEMENTS IN THE
CHEMICAL FRACTIONS FROM FERGUSSON *et al.*[18]

Element (µg/g)	Chemical fractions				
	Exchange fraction	Carbonate fraction	Fe-Mn oxide fraction	Organic fraction	Residual fraction
Mn	1.7	7.8	36.9	2.6	51.1
Fe	0	0.3	10.8	1.3	87.5
Cu	1.3	8.6	11.3	53.2	25.6
Zn	3.4	30.2	50.8	9.1	6.6
Pb	1.9	34.1	44.2	7.1	11.2

TABLE-3b
DISTRIBUTION OF SOME TRACE ELEMENTS IN CHEMICAL
FRACTIONS FROM HARISON *et al.*[19]

Element (µg/g)	Chemical fractions				
	Exchange fraction	Carbonate fraction	Fe-Mn oxide fraction	Organic fraction	Residual fraction
Mn	7.30	30.00	5.90	76.1	20.5
Fe	8.80	209.0	196.0	31.5	19.9
Cu	18.7	665.8	511.3	110	162.2

Copper (29, 35 %) with carbonate and Fe-Mn oxide fractions respectively. Fergusson *et al.*[17] have extracted copper from organic fraction with a percentage 53 %, Harison *et al.*[19] have shown that 55 % of Cu is extracted from organic fraction, a percentage that is compared with that reported by Gibson and Farmer[20] who have shown that 46, 44 % of Cu in soil and street dust samples is extracted from the residual and organic fractions, respectively.

The study of soil and street dust from Khartoum state has shown that (33, 25 %) of zinc extracted from the carbonate and Fe-Mn oxide fractions in comparison wit Fergusson *et al.*[17] results, who found (70, 95 %) of Zn is extracted from carbonate and Fe-Mn oxide fractions respectively. Harison *et al.*[19] have mange to extract (44, 42 %) of Zn from carbonate and Fe-Mn oxide fractions, respectively, while Fergusson *et al.*[18] have reported 50 % of Zn extracted from Fe-Mn oxide fraction. Gibson and Farmer[20] have obtained (45, 28 %) of Zn in soil and street dust samples extracted from the residual fraction respectively.

TABLE-3c
DISTRIBUTION OF SOME TRACE ELEMENTS IN CHEMICAL FRACTIONS FROM M.J. GIBSON AND J.G.FARMER[20] DATA

Element	Source	Chemical fractions				
		Exchange fraction	Carbonate fraction	Fe-Mn oxide fraction	Organic fraction	Residual fraction
Cu	Soil	2	2	9	41	46
	Street dust	11	4	8	43	31
Zn	Soil	3	7	13	29	43
	Street dust	10	23	19	26	26
Pb	Soil	2	11	51	19	17
	Street dust	13	28	27	14	13

Present study has reported 30 % of lead (Pb) to be extracted from exchangeable fraction. Fergusson *et al.*[17] have extracted (65, 85 %) Pb from carbonate and Fe-Mn oxide fractions respectively. Fergusson[18] obtained 45 % of Pb extracted from Fe-Mn oxide fraction. Harison *et al.*[19] have been able to extract 45 % of Pb from carbonate fraction. Gibson and Farmer[20] have shown that (54, 29 %) of Pb in soil and street dust samples has been extracted from Fe-Mn oxide and carbonate fractions, respectively.

Tokalioglu *et al.*[21] (Fig. 2) found that the zinc in the street dusts is strongly associated with the exchangeable and bound to carbonates phase (33.2 %), while 29.7 % of Zn is related to the Fe-Mn oxides phase. Organic/sulphide fraction accounts for about 20.9 % of Zn in street dust. Zn in the residual fraction was found as 16.2 %.
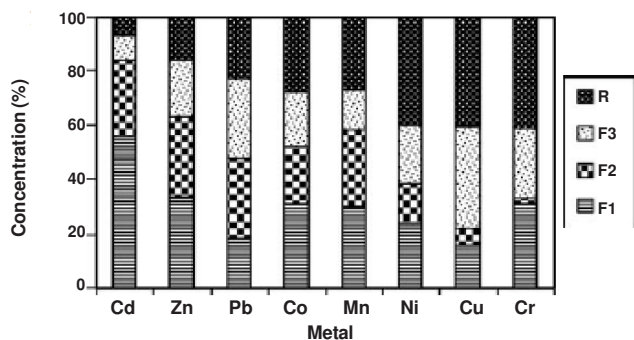

Fig. 2.   Chemical fractionation patterns of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in the street dusts. Serife Tokalioglu *et al.*[21]

The chemical association of Cu within the street dusts is dominated by the residual (41 %). Although the proportions of Cu present in different fractions varied considerably. Its association in the non- residual fraction was dominated by the organic/sulphide phase (36.6 %), the exchangeable and bound to carbonates phase (15.8 %) and the Fe-Mn oxides phase (6.5 %). Pb is partitioned equally between the reducible and oxidizable phases. The percentages of lead in reducible and oxidizable fractions in street dusts are 29.2 and 29.7 %, respectively. The Pb percentage of fraction 1 is 18.2 %. The adsorption of Pb cations on the hydrous (amorphic) oxides of Fe/Mn is considered as a reasonably universal fixation mechanisms and the ability of lead to form organic complexes[22].

Chromium was primarily bound to the residual fraction, accounting on average for 41.4 % of total Cr. This result is probably due to the preferential incorporation of Cr into the silicate lattice. The remaining Cr exhibits a partitioning pattern that is distributed between fraction 1 (30.8 %) and fraction 3

(25.7 %). The proportion of Cr in the reducible fraction was fairly low (2.1 %). Fig. 3(a-e) show the extracted component loading (absolute values that explain the correlation between a variable and component) for each element.

For the exchangeable fraction it is observed that Cu, Zn and Cr show high loading in component 1 and this can be attributed to tannery and industrial areas emission. High loading were observed for Fe and Mn in component 2, which can be associated with soil dust source. For carbonate fraction, Cu and Zn have high loading in component 1 and this also may be from industrial areas emission. In component 2, Mn and Pb show high loading and this may be due to car emission.
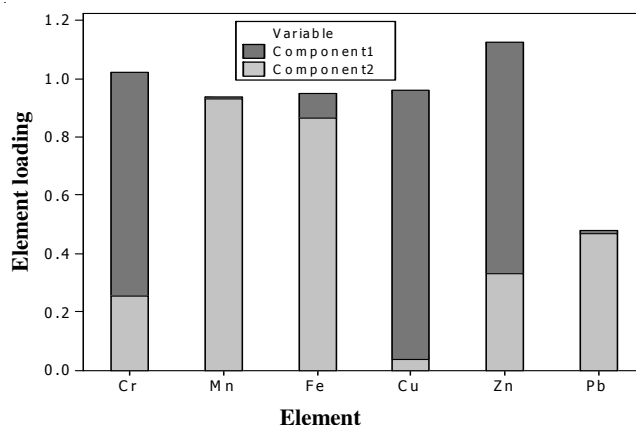

Fig. 3a. Varimax rotated component loading for the trace elements concentrations in Khartoum soil and street dust in exchangeable fraction
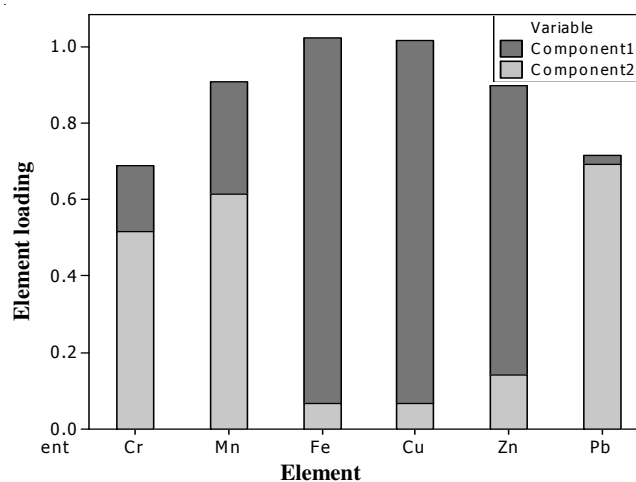

Fig. 3b. Varimax rotated component loading for the trace elements concentrations in Khartoum soil and street dust in carbonate fraction
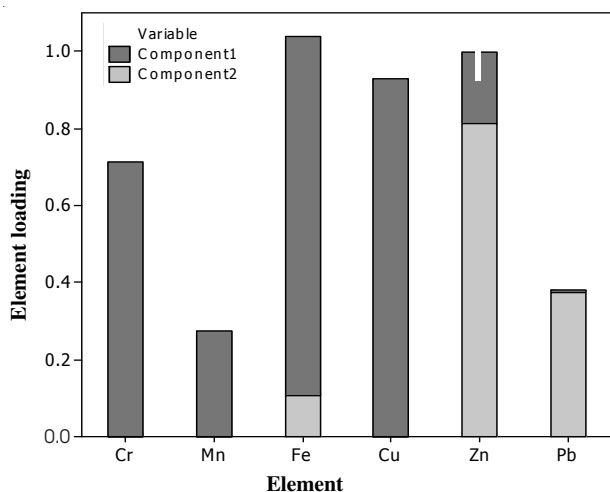
Fig. 3c. Varimax rotated component loading for the trace elements concentrations in Khartoum soil and street dust in Fe-Mn oxide fraction
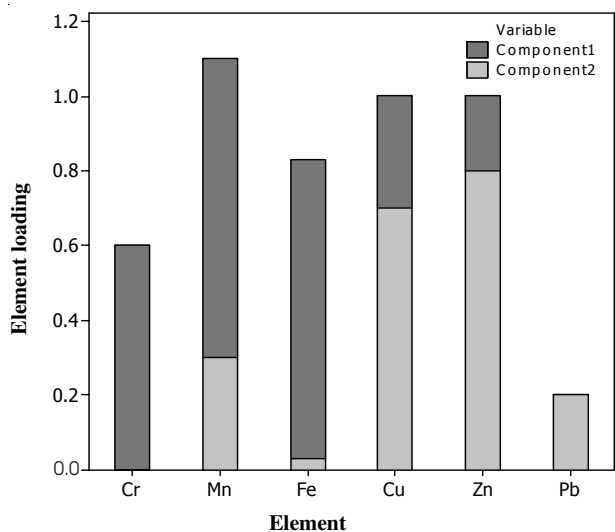

Fig. 3d. Varimax rotated component loading for the trace elements concentrations in Khartoum soil and street dust in organic fraction.
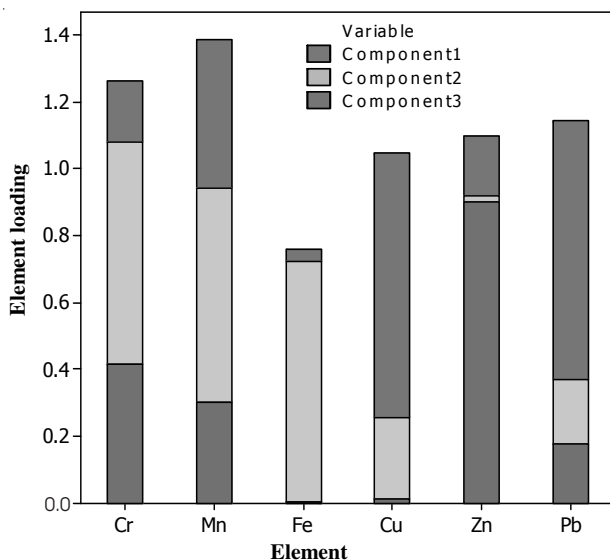

Fig. 3e. Varimax rotated component loading for the trace elements concentrations in Khartoum soil and street dust in residual fraction

In Fe-Mn oxide fraction the high loading of Cu, Zn and Cr in component 1 and Cu, pb in component 2 can be observed and it may be due to the same sources mentioned above. In organic fraction also Fe, Cu and Cr show high loading in component 1 and Zn, Pb in component 2. For residual fraction, Fe, Cu and Cr are loading in component 1 Cu in component 3.

Conclusion

The study showed scattered values of trace elements for samples collected from street dust and soil and it was in accordance with expected pollution sources. Fractionation gives acceptable values for the fractions and the bulk. The comparison between soil and street dust samples and control showed that the elements distributed in the chemical fractions in the way that reflects the source type, mobility and bio availability of these elements. Principle component analysis showed high loading for the elements that come from the same sources.

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