DETERMINATION OF ELEMENTAL COMPOSITION OF AIR PARTICULATES AND SOILS IN KHARTOUM AREA

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ABSTRACT

Investigations were carried out for elemental composition of air particulates in the background air and near roadsides in Khartoum area. Investigations were also performed for the elemental composition of soils at the same locations. A cyclone and a dichotomous virtual impactor were used to measure the air particulates. The cyclone was adjusted to collect particles having an aerodynamic diameter of 2.5μm. The virtual impactor, through its fine channel, was capable of collecting airborne particles with an aerodynamic diameter of 2.5 μm. Energy Dispersive X-Ray Fluorescence (EDXRF) analysis was used to study the elemental concentrations of the air and soil samples. The analysis of the results indicated that all elements in the proximity of roadsides have elevated concentrations compared to the background air levels. Enrichment factors were calculated relative to crust rock and Khartoum soil. The results showed that the elements K, Ca, Ti, Fe, and Sr in the aerosols have their origin from the soil, while the elements Zn, Ni and Pb have their source from automobile emissions. The results also indicated a correlation between lead and bromine. The lead to bromine ratio was found to be within the range of those derived from vehicular exhaust, and in good agreement with the ratios obtained from some other countries.

INTRODUCTION

Urban air particulates, which originate from various sources such as energy consumption and emissions from the transportation sector, are of concern because of their health effects. Air quality standards for particulate matter (PM) have been established in many countries based on PM10, a size-specific standard. PM10 is defined as the fraction of PM captured with 50% efficiency at 10 μm, and greater efficiency at smaller sizes. It has been shown in many studies that the elevated levels of PM10 are linked to increased adverse health effects. Particulate matter having diameter 2.5μm and below, referred to as PM2.5, is a sub-size of PM10. It is captured with 50% efficiency at 2.5 μm. It can penetrate more deeply in the breathing system and can have serious health effects as well (Hinds 1982, Wahlin *et al.* 2001, McLellan 2002).

A major source of urban air particulates is emission from vehicular traffic which has been considerably increasing in the past decades. Other particulates may have their origin in the soil particles that build up through the process of soil re-suspension or mobilization.

Two mechanisms account for the traffic contribution to the roadsides airborne particulates. Re-suspension or mobilization of the soil particles by traffic has the larger part of the total mass of street dust, especially when roads are unpaved. The other mechanism is the direct emission from vehicles. To investigate the influences of the two sources on the roadside air particulates, the Enrichment Factors (EF) for some elements were calculated. This is needed to characterize whether the measured concentrations are originating from the soil re-suspension or are enhanced by automobile emissions. Ti and rock of crust material have been commonly used in calculations of EFs (Djupstrom 1995, Chimidza *et al.* 2001).

Crust rock was used as reference material for

the calculations of the EFs for Khartoum aerosols. This is because Khartoum area lies in the southern belt of the Sahara desert and, it is thus expected to be influenced by Sahara soil particulates.
The EFs have been calculated using the relation:
$EF(x) = (C_x (a) / Ti (a)) / (C_x (ref) / Ti (ref))$

where EF(x) = enrichment factor for the element x
C_x (a) = concentration of the element x in the measured aerosols
Ti (a) = concentration of Ti in the measured aerosols
C_x (ref) = concentration of the element x in the reference material
Ti (ref) = concentration of Ti in the reference material

Impactors and cyclones are instruments widely used for separating particles over a desired diameter range. In the virtual impactor used in this study, the airborne matter is passed through a nozzle and then forced to bend abruptly at 90^O by an impaction surface. Particulates having high inertia will be collected through the impaction plate. Particles with low inertia will follow the stream of the air and will be collected on a different medium. A cyclone removes particles larger than a desired size range from the drawn air by means of centrifugal forces. The cut-off of the cyclone changes with different flow rates. The flow rate could be adjusted to get different cut-off diameters of particles by using limiting orifices. Particles with higher inertia are collected on the inner walls of the cyclone and eventually fall down to a grid pot, while particles with aerodynamic diameters smaller than the cut-off size follow the air stream (Hinds 1982).

EDXRF, which was used in this study, has been used widely as trace analytical technique for the environmental samples. It is known to be a non-destructive analytical technique, with multi-element capability and simple sample preparation. Analysis of heavy elements in aerosols by EDXRF is performed by measurement of a collection of the particulates on filters when a definite volume of air has been passed through the filters (Eltayeb 1993).

The possible sources of particulate matter in Khartoum area are the pollutants generated from the anthropogenic sources and human activities, such as vehicle emission, biomass burning and the growing industry (textile, cement, petroleum refining, tanning, electricity production, etc.). In addition to the anthropogenic air particulates, the wind blown dust from Sahara desert located in the north part of Sudan was expected to exert some influence on the composition of air particulates in Khartoum area.

Some previous studies have been performed for particulate pollutants and vehicle traffic emissions in Khartoum area (Hassan 1984, Eltayeb 1993, Hassuna *et al*. 1998). In the study by Hassuna *et al*. (1998), measurements were carried out for elemental concentrations in Khartoum aerosols, but the study did not segregate particles. Also the study lacked information on concentrations of the important element Pb. The present study aimed to identify the sizes and the possible sources, as well as to determine the concentrations of the different elements in the airborne particles in Khartoum area. This was considered a fundamental step in the control of their presence and hazards. Some investigations were also made for Pb concentrations in soils near some road-sides in Khartoum city.

MATERIALS AND METHODS

Selected locations

In this study airborne particulates were sampled at ten different locations near road-sides in the center of Khartoum. Another site inside the central campus of the University of Khartoum was selected to represent the general background air of the city. The ten locations near the roadsides were selected to represent the high traffic density roads near the different types of

activities, commercial as well as residential. To investigate accumulation of atmospheric lead concentrations as a historical marker for automobile emissions, soil samples were taken from different distances and depths near the road-sides. Fig.1 shows the selected locations for aerosols and soil samples.

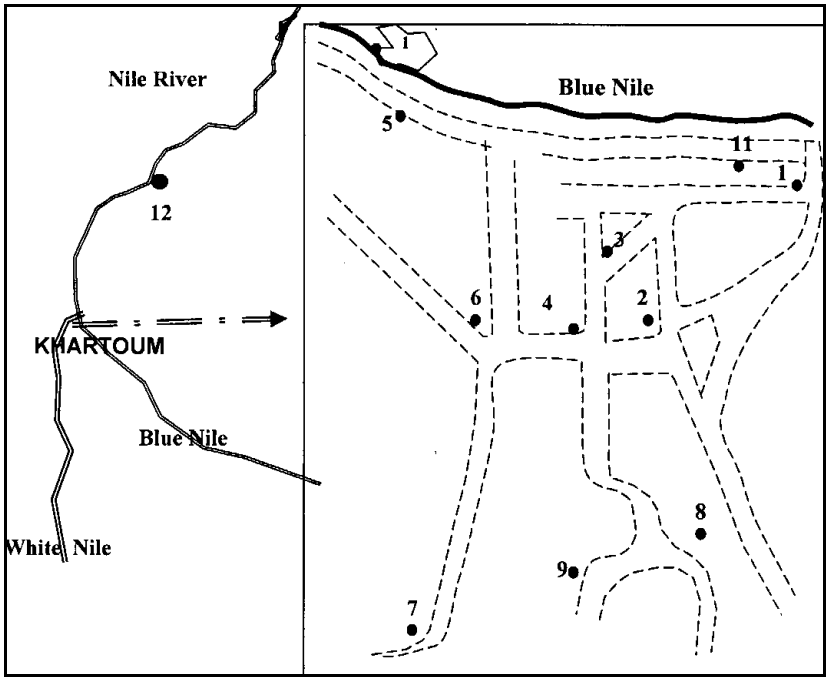

Figure 1: Locations of the atmospheric and soil samples in Khartoum area (1 Gamaa St, 2 Mack Nimir St 3 Atbara St 4 Gasr St 5. Nile St 6 Hurria St 7 Hurria St 8 Amarat St 9 Sahafa Zalat St 10 Tuti Island 11 U of K 12 120 120 km Nrth of Khartoum)

Aerosol samples

The sampling instruments used in this study were a cyclone for near road-sides sampling and a dichotomous virtual impactor for the background air measurement (Carlsson 2000, Eltahir 2003).

The cyclone was placed with the sampling inlet approximately at 1.5 m above the ground level, and at one meter from the edge of the roadside. The flow rate was adjusted to 2.5 l/min to select particles of cut-off diameter similar in size to particles collected through the fine channels of the virtual impactor. Then it is possible to compare the road-side aerosols collected by the cyclone with the particulates collected from the general background air by the fine channel of the virtual impactor. Four samples were taken from each location. The sampling period for one sample was five hours. The study was usually carried out two times a day, during the morning and afternoon periods. The collection was conducted on roads with dense traffic, but away from industrial emissions.

The dichotomous virtual impactor was placed on the top of a building 3m high. It separates the collection of air particulates of sizes 2.5 μm by the fine channel and of sizes 10 μm by the coarse one. Thus both fine particulates and coarse ones were collected on the filters. The filters in the

impactor were changed every twelve hours during the day period.

The collection by the two instruments was performed using ring Teflon membrane filter (Millipore), 37 mm in diameter, with pore size 2 μm. The filter samples were then weighed and measured by EDXRF.

Soil samples

The soil samples were collected at the same locations as the air particulates. They were taken at distances of 1, 5 and 10m from the edge of both sides of the road, and at depths of 0.1, 0.2 and 0.3m. To calculate the enrichment factor (EF) for Khartoum aerosols relative to the north of Khartoum Sahara soil, 10 soil samples were collected from a location 120 km north of Khartoum. All samples were then kept in air tight plastic bags for laboratory analysis. Two methods were used to prepare soil sample for EDXRF analysis. In the first method, each sample was poured and evenly distributed on a very thin and clean cello-tape. The cello-tape was initially checked for contamination and was used only when free from any contaminants. In the second method, parts from the same samples were homogeneously mixed, dried by heating at 100°C for two hours, and then ground to powder form. Then they were pressed into pellet form of one inch diameter and about 1g mass, using a pressing machine at 15 ton. The samples were then weighed and measured by EDXRF.

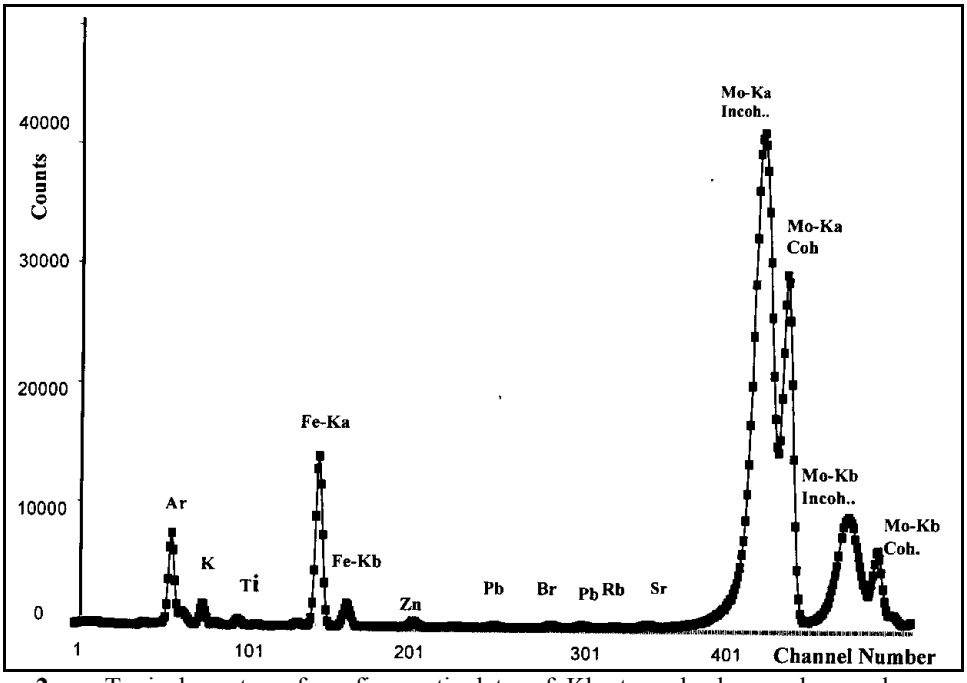

Figure 2: Typical spectrum from fine particulates of Khartoum background aerosols

Analytical methods

Use was made of two different spectrometer systems for the analysis of the samples. The aerosol samples and soil samples on cello-tape were measured using a tube excitation EDXRF spectrometer system described elsewhere (Standzenieks and Selin 1979, Eltahir 2003). The soil samples in pellet form were measured using Cd-109 EDXRF spectrometer system at the University of

Khartoum, Sudan (Habbani and Salih 1999). Emphasis in the isotopic source method was on the determination of the elemental concentration of Pb, while in the tube excitation method multi-element analysis was performed. The data from the measurements was analyzed using the computer program AXIL (Van Espen et al. 1986). Fig. 2 shows a typical spectrum of the fine particles in the background aerosols of Khartoum city. Details of the analysis procedure of the air particulates are described elsewhere (Eltahir *et al.* 2005). The data from the Cd-109 spectrometer system were converted to Pb concentrations using a calibration obtained by use of standard solutions of lead compounds.

RESULTS AND DISCUSSION

Aerosol elemental concentrations

The elemental range, mean concentration, the standard deviation (SD) and the median concentration of the background air particulates and near road-sides air particulates are presented in Table 1. The results of the elemental concentrations of the road-sides collections were obtained from computing an overall mean value out of the individual mean of the analytical results of the ten locations. The background elemental mean concentrations were obtained out of the analytical results of the impactor's fine channel. The high value of sample to sample SD is due to variations of the meteorological parameters e.g. wind and dust. Median concentration was presented in the Table because the outlier values have less effect on its value. In the Table some elements have been excluded because of being below detection limits in more than half of their analytical results e.g. Cr and V.

It can be seen from the Table that all elemental concentrations in the road-sides airborne particulates have relatively higher levels than that of the background. These seem to reflect an influence of urban and natural sources on the road dust. Two distinct groups of elements could be characterized according to the difference in the level of the increase. The increment of the concentrations of the elements K, Ca, Ti, Mn, Fe, and Sr (group1) is much less than of the elements Ni, Zn and Pb (group2). However, in both groups the high levels of concentrations in the road-sides could be attributed to traffic emission.

Fig.3 is a comparison between the mean elemental concentrations for some elements of the road-sides particulates and the fine particles of the background aerosols.

Table 1: Elemental range, mean (SD) and median concentrations of some elements in the background air and roadsides of down town Khartoum

EI	Min-Max (ng .m-3)		Mean (SD) (ng .m-3)		'Median (ng .m-3)	
	Background	Roadside	Roadside(SD)	Background (SD)	Roadside	Background
K	220-750	830- 1620	1100(100)	410(150)	1100	340
Ca	490-2600	560-5800	1800(650)	1000(600)	1300	810
Ti	60-390	80-380	200(60)	150(150)	170	93
V	DL	60-65	60(10)	DL	65	DL
Mn	12-80	40-100	68(10)	30 (30)	60	20
Fe	600-3400	420-5300	2700(900)	1400 (1000)	2500	915
Ni	2-5	50-120	80(16)	3 (1)	70	2
Cu	1-4	DL	200(30)	13(6)	DL	2
Zn	8- 25	100-320	15(1)	4(2)	190	11
Br	2-8	14-15	15(1)	4(3)	15	3
Sr	3-16	14-30	22(4)	7(4)	22	5
Pb	4-11	30-90	49(15)	6(2)	49	5

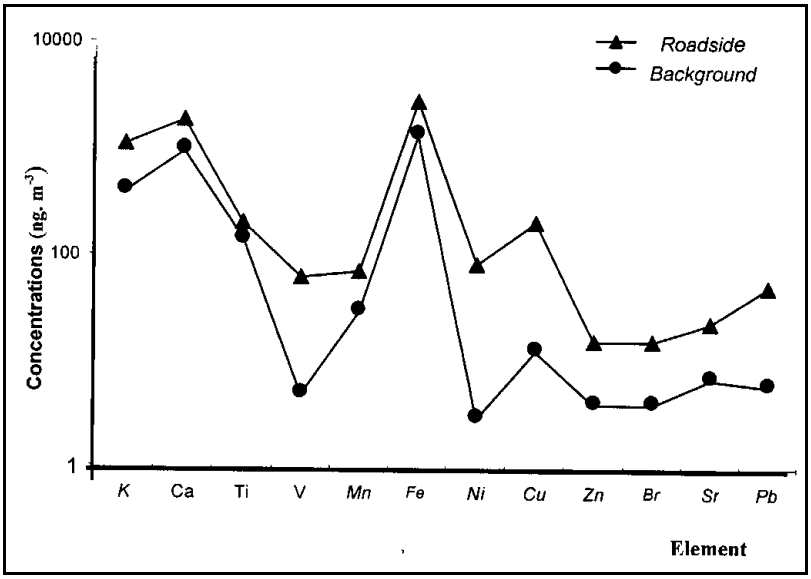

Figure 3: Elemental mean concentrations for some elements in background and near road-side aerosols in down town Khartoum

Soil elemental concentrations

The aim of the soil analysis was to study the correlation of some elements in the aerosols to their concentrations in the soil. The expected correlation was based on the assumption that the presence of the elements derived from the soil in an aerosol would be in the same proportion as in the soil. Near road-sides the traffic would have influence on both particulates concentrations and the soil.

Table 2 shows the enrichment factors for some elements in the background air and near road-sides of Khartoum relative to the southern belt of Sahara desert 120 km north of Khartoum. The concentrations of the continental crustal rock were obtained from Taylor and McLennan (1985), denoted as (T&M) and from Rundick and Fountain (1995), denoted as (R&F). Fig. 4 shows a comparison of the EFs for some elements in background aerosols and road-sides in down town Khartoum. The lead concentrations decreased with distance away from the road-sides. in the upper layer of the earth surface near road-sides They were found to be in the range (10 - 50) μg/g in the upper layer of the earth surface near road-sides. Such concentration levels of Pb are in the normal range of Pb in the soil.

Roadsides particulates

The analytical results obtained from the soil samples from different locations near road-sides and from the southern Saharan belt, 120 km north of Khartoum, were used to calculate the EFs. The purpose was to examine the relationship between elemental concentrations in the soil and airborne concentrations. As can be seen from Table 2 the EFs for elements in group1 in the road-sides aerosols have values higher than the values obtained for group 2. Although the re-suspension of the soil raised the concentration levels of the two groups, the highly enriched elements Ni, Zn and Pb in the road-sides are thought to have their origin from direct vehicles emission as well. It is known that Pb has been used as an anti-

knock agent in automobile fuel. Ni could originate from oil combustion, while Zn compounds have been employed as anti-oxidants and as detergent/dispersant improvers for lubricating oils (Ogunsola *et al.* 1993).

Table 2: The EFs for some elements in background air and near roadsides of Khartoum, relative to north of Khartoum Sahara desert soil and to the continental crust. (*NA = not available: either in the reference crust results or not detected in the present work)

	EF (Crust/ R&F)		EF (Crust/ T&M)		EF (Sahara desert)	
Element	Back-ground air	Road-side	Back-ground air	Road-side	Back-ground air	Road-side
Si	0.66	0.49	0.87	0.66	NA*	NA
K	1.7	3.4	3.2	6.5	2.5	5.1
Ca	0.61	0.83	0.68	0.92	3.2	4.3
V	NA	9.0	NA	7.6	NA	NA
Cr	0.94	NA	0.78	NA	NA	NA
Mn	1.1	1.8	0.77	1.3	1.7	2.9
Fe	0.76	1.1	0.71	1.0	3.0	4.3
Ni	1.7	33	1.0	21	3.6	71
Cu	2.3	NA	0.96	NA	2.3	NA
Zn	5.0	57	5.6	67	3.6	43
Rb	0.48	NA	1.1	NA	0.4	NA
Sr	0.60	1.4	0.97	2.3	1.7	4.1
Pb	13	81	27	165	8.8	54

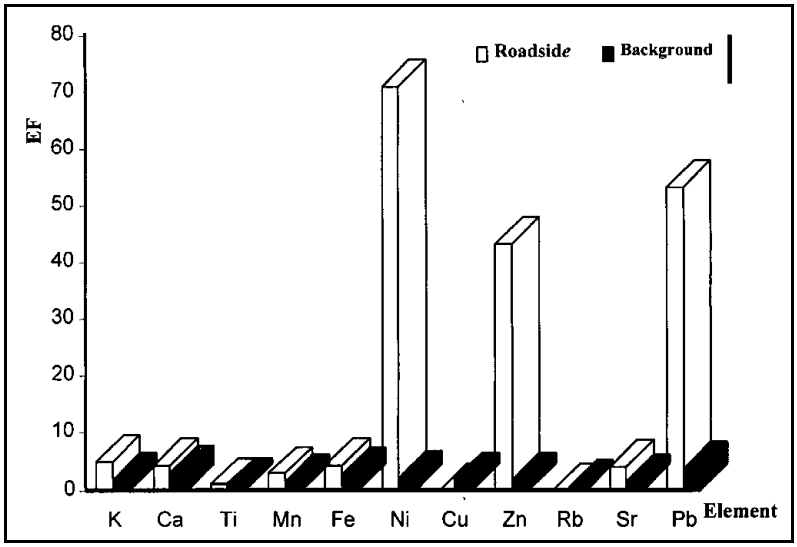

Figure 4: Comparison of the EFs for some elements in road-sides and background aerosols of down town Khartoum

Lead attributed to traffic

Historically lead has been the most reliable tracer of traffic. To investigate the source of road-sides lead, the bromine-to-lead ratio

was calculated. In the proximity of road-sides, for the aerosols derived from direct car exhaust, the same ratio between Br and Pb was found as for the anti-knock agent of the fuel. This ratio was used to trace out vehicular lead concentrations in the atmosphere (O'Conner *et al*. 1977). Table 3 shows a comparison of Pb/Br ratio for Khartoum with some other countries (Faiq and Abdalla 1988, Ogunsola 1993, Bennet et al. 2005, Moloi *et al*. 2002). Although small differences occur, there is generally a good agreement between the values for the different countries. Figure 5 shows a good correlation between Pb and Br in Khartoum aerosols This strengthens the suggestion of their origin from automobile emissions.

Table 3. Comparison of Pb/Br ratio in Khartoum with other countries in the region

Country	Pb/Br
Khartoum (Background, atmospheric)	2.43
Khartoum (Road side, atmospheric)	3.3
Lagos (Nigeria, atmospheric)	2.24
Iraq (atmospheric)	2.43
Dar Es-Salaam (Tanzania, atmospheric.)	2.7
Gaborone (Botswana, atmospheric)	2.0

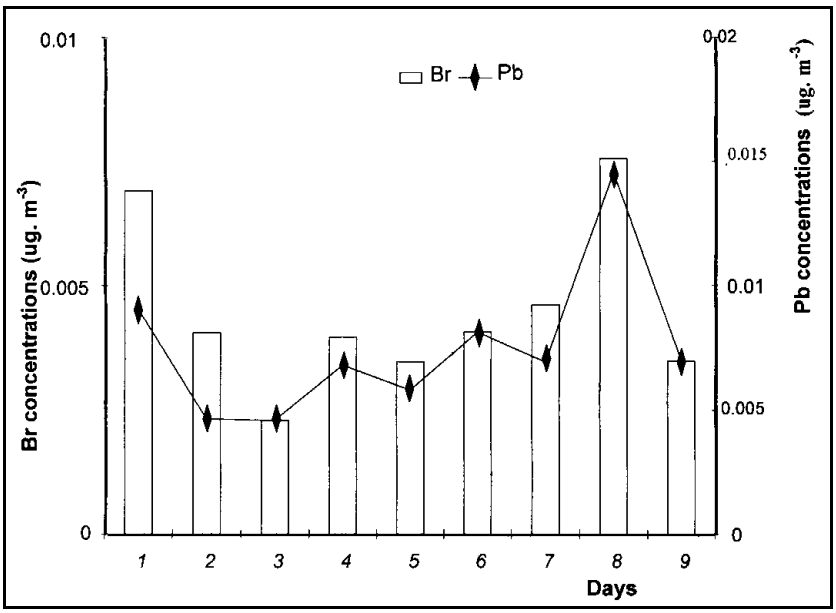

Figure 5: Concentration profiles of Pb and Br in Khartoum aerosols

CONCLUSION

The analytical and the statistical results from this study indicated elevated concentrations levels for some elements near road-sides compared to the background values as expected. The influence of traffic to the street dust in Khartoum city is characterized by elevated levels of the elements Zn, Ni and Pb, which have been highly enriched near roadsides. Their enhancement appears to originate from the mobilization and re-suspension of the surface soil near roads and from direct automobile emissions.

The Pb/Br ratio in Khartoum atmospheric particulates is in good agreement with ratios obtained from some other countries in the region. The strong correlation observed between Pb and Br indicated that the road-sides lead source is automobile emissions.

The study revealed that the concentrations of the soil lead (10-50 μg/g) are of little health concern because they were less than the prescribed ambient air quality standards.

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