Heavy Metal Levels in the Soils of Riyadh City, Saudi Arabia

S.M. AL-SHAYEB

Riyadh College of Technology, Department of Chemistry P.O. Box 42826, Riyadh 17551, Kingdom of Saudi Arabia

The metals content (Pb. Zn. Cu. Cr. Ni and Li) of surface and subsurface soils was determined in Riyadh city. A total of 303 surface soils and 303 corresponding subsurface soil samples were collected at intersection points of a 1 × 1 km grid covering the whole city. Metal levels were investigated in relation to population density, prevailing wind direction, land topography and the structure of the buildings in the city. The levels of Pb, Zn and Cu were found to be elevated in the urban areas (city centre), which are correlated well with the population density. Lead, zinc and to a lesser extent copper distribution in surface soils were affected by the prevailing winds. Lead levels were attributed to the automobile emission whereas Zn and Cu were found to be associated more with the industrial locations than in residential areas. Surface to subsurface ratio results showed Pb, Zn and Cu were largely concentrated in the upper surface soils indicating the atmospheric deposition as the main source of such metals.

Key Words: Heavy metal levels, Soils, Riyadh city, Saudi Arabia.

INTRODUCTION

Soil contamination by heavy metals resulting from the emission of fumes and smoke from transportations and industrial plants is recognized as a major problem in different countries. Heavy metals are indicated in many studies as one of the major environmental problems of their persistence in soils^{1, 2}. Kung and Ying³ determined Pb, Zn, Cr, Cd and Hg concentrations in soils of Bashan-Wusong area, Shanghai. Their results showed that soil pollution occurred predominantly around the industrial complex, which was attributed to the industrial activities. The content of Pb, Cd, Cr, Hg and As in soils from different industrial areas was investigated by Kafka and Kuras⁴. Their results show that the concentration of heavy metals in some areas was so high that these soils need immediate decontamination or at least some remediation measures. McGrath⁵ measured the concentrations of Pb, Zn, Cu, Ni, Hg and Cd in Irish soils. The metal content in soils from an area with modern industrial development was generally indicative of low pollutant inputs. The distribution of Pb, Zn, Cu and Cd in topsoils of Osnabruck was studied in relation to land use by Bloeman et al.⁶ The extremely high values around a metalwork factory in Widukindland were a striking feature.

Their results were recorded in the form of soil pollution maps, which make it possible to identify unusual polluted areas. In Spain, Sanchez-Camazano et al.⁷ determined lead content of soil from 16 urban gardens of Salamanca. The mean lead concentration found (43.1 µg g⁻¹) was 2.6 times higher than that in uncontaminated soils.

Heavy metal in surface soils can be determined in order to monitor aerial metal pollution, metal contamination in the soil, and to study the spatial distribution of metal pollutants. Surface soil can be analysed to establish baseline data for metal levels in soils and to investigate the effects of certain sources of metal pollution. including point sources (e.g., power plants, oil refineries and smelters) and line sources (e.g. roads and highways). Goodman and Roberts⁸ concluded that soils could be used as indicators of aerial metallic burdens. They described this method as much more rapid, inexpensive and probably more meaningful than spot sampling of air by filtration, for which prohibitive resources are needed for a few months operation. Tam et al. 9 used surface soil (0-1 cm) in a survey of roadside metal contamination in Hong Kong and found a significant correlation between traffic volume and Pb, Cu and Zn concentrations. This suggested that metallic contamination of roadside soil might be due to direct deposition of metals derived from vehicles and their exhausts and/or the relocation of metals deposited on road surface. Ho and Tai¹⁰ used the surface soil (0-2 cm) to monitor lead and copper at two roadside sites in Hong Kong from 1978 to 1987 and found that lead decreased as a result of the reduction of lead content in petrol. In Egypt, El-Sherif and Hanna¹¹ analysed both surface and subsurface soils for lead and cadmium contents. They regarded their study as providing baseline data, which can be used in the future to evaluate any changes in the levels of these metals.

There are very few studies about the metal pollution in Rivadh city. El-Sahaf¹² has evaluated some atmospheric pollutants in seven places in Riyadh city. Ahmed et al. 13 investigated metal concentrations in the dust of Riyadh. The concentrations of Pb, Cr, Cu and Zn were 305.4, 205.9, 183.4 and 486.8 (µg g⁻¹) respectively. Al-Rajhi et al. 14 investigated the concentrations of Cd, Cr, Cu, Ni, Pb, Zn and Li of outdoor and indoor dusts in Riyadh city.

All the above studies investigated the metal pollution in deposited and suspended particulates. But apart from the work done by Al-Shayeb and Seaward¹⁵ and Al-Shayeb¹⁶, investigating the metal distribution in soil profiles and metal content in soils of the industrial locations in Riyadh city respectively, nothing is known about the soil metal content in Riyadh city. This shows the extreme need for this extensive monitoring program which is covering the entire city of Riyadh to reveal the metal contents and show their distribution patterns which will be of great importance in identifying hot-spots and investigating sources of the pollutants.

EXPERIMENTAL

Sample collection

This area covers the city of Riyadh, which was divided according to the population density distribution: urban, suburban, and rural areas. To achieve

spatial coverage of the entire city, intersection points of a 1×1 km grid covering the whole city were selected as sample sites. All sites were at least 50 m away from a main road to ensure that the topsoil was not contaminated directly by vehicle emissions. In situations where it was impossible to collect a sample or major source appeared likely to provide too great a contribution (e.g., within 30 m of a major road) a substitute sample was taken at 50 m distance, in the direction of one of the four main compass points in the preferential order of North, East, South, West. A total of 303 surface soils (0-3 cm) and 303 corresponding subsurface soil samples (5-10 cm) were collected (Fig. 1). Samples were collected using a stainless steel trowel, and placed in two separate bags. In order to reduce the possible effects of variation in the trace element concentrations over the vicinity of the sampling location, four surface and two subsurface soil samples were taken at the four principal compass points at the circumference of a circle of 1 m radius centred on the first sample point. These samples were bulked in the same two bags. At some locations, the soil was too dry and hard; in such cases, the subsurface soil was loosened with a stainless steel geological hammer and soil removed with the trowel.

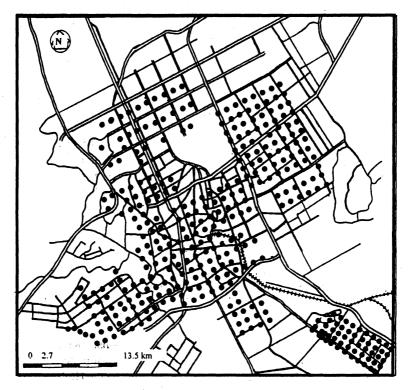


Fig. 1. Riyadh: soil sample locations, excluding main roads and highways

Sample preparation

All samples collected from the field were thinly spread on polyethylene sheets and allowed to dry in air at ambient temperatures They were then desegregated

and passed through a two-millimetre aperture nylon sieve. A subsample of 25 g was taken from each sample by coning and quartering and packed in clean self-sealing plastic bags with their field numbers. All soil samples were then dried at 105°C to a constant weight and stored in clean plastic containers with their distinctive laboratory numbers.

Measurement of soil organic matter and pH

Bradley and Cox¹⁷ stated that pre-treatment of soil samples at 430°C prior to acid extraction is sufficient for the pyrolysis of organic compounds and provides a good estimate of the organic content of soils. Pre-treatment at 430°C also permits a good estimate of the concentration of metals in the soil. The organic content of the soil samples was therefore determined gravimetrically by the loss in weight of the sample after ignition at 430°C. The pH was measured for the soil samples using a pH-meter.

Sample digestion techniques

Due to its reliability, simplicity, flexibility and wide use hy many researchers, aqua regia was used in this work to digest soil samples.

Subsamples (1 g) were weighed into Pyrex test tubes, to each of which 10 mL of aqua regia (3 HCl: 1 HNO₃) was added. The tubes were then placed in a controlled heating block and the samples digested for 1 h at 60°C, 2 h at 80°C, 2 h at 105°C and 3 h at 120°C, successively. After cooling, the samples were centrifuged and made up to volume. Metal contents were then determined by flame atomic absorption spectrometry (Perkin-Elmer model 1100).

Analytical precision and accuracy

In order to obtain acceptable results during the analysis of soil samples, the following procedures were employed for precision and accuracy.

The analytical work was divided into batches; each batch comprised 50 samples. To assess the precision, 20% of the samples in each batch were randomly chosen and duplicated. The precision is usually expressed as the % coefficient of variation (CV). Generally, the CV for all the metals determined was < 10%.

The accuracy is evaluated by analysing certified reference materials and quoting the percentage recovery. Accuracy in this work was checked by including samples of Buffalo River Sediment (SRM 2704) and BCR Reference Soil (No. 141, calcareous loam) with each soil batch.

RESULTS AND DISCUSSION

Levels of metals and distribution in Riyadh's soils: Riyadh city was divided into urban, suburban and rural zones, on the basis of population density, according to the rnap of population distribution provided by the High Commission for Development of Arrivadh (HCDA) The urban zone was defined by area with a population density of 50 or more persons per hectare, encompassing an area comprising mostly commercial and industrial properties, some houses, a dense street network and a large traffic volume. The suburban zone was defined as an area with a population density of 1-49 persons per hectare, comprising mainly

residential areas with some light industry and some commercial areas. The area of the city containing less than one person per hectare was regarded as rural area and included scattered houses and farms.

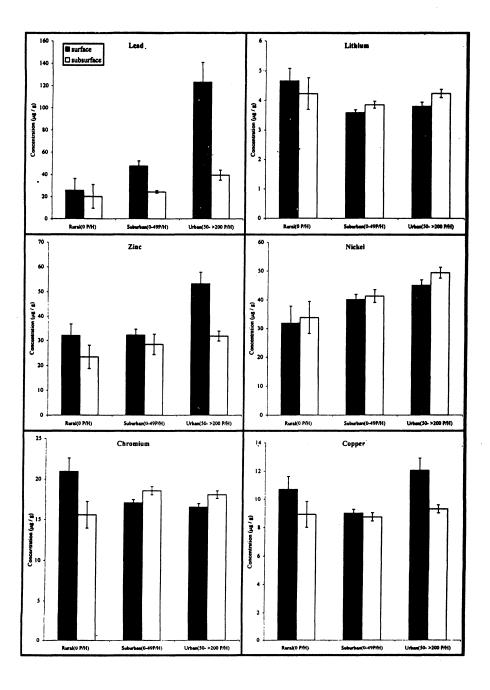
Fig. 2 shows the metal variation in surface (0-3 cm) and subsurface (5-10 cm) soils according to population density. The relationship between wind direction and metal distribution in Riyadh city is shown in Fig. 3.

Lead: The concentration of lead in the surface soil samples varied from 6.6 μ g g⁻¹ to 1462 μ g g⁻¹ with an average value of 80.75 μ g g⁻¹, whereas its concentration in subsurface soil samples ranged from 4.0 μ g g⁻¹ to 570 μ g g⁻¹ with an average value of 31.04 μ g g⁻¹. From the spatial variations it can be seen that lead levels are strongly associated with population density and the city centre where human activities and automobile emissions are very high. This agrees with the findings of other researchers^{18, 19}, who found that most of deposited airborne lead originated from the combustion of leaded gasoline by automobiles.

- (a) Urban area: In this area lead levels in surface soil varied from 18.2 $\mu g g^{-1}$ in Hai AI-Zahrah in the west of the city to 1462 $\mu g g^{-1}$ in the city centre, with an average value of 123.28 $\mu g g^{-1}$. Lead levels in subsurface soils ranged from 4.0 $\mu g g^{-1}$ in Hai AI-Zahrah to 570 $\mu g g^{-1}$ in the old airport area, with an average value of 39.56 $\mu g g^{-1}$. Lead levels in surface soils proved to be the highest of those metals investigated (Fig. 2).
- (b) Suburban area: The lead levels found in surface soil samples in this area varied from 9.20 μ g g⁻¹ in Hai Al-Swaidi Al-Gharbi in the west of the city to 521 μ g g⁻¹ in Hai Al-Aziziyagh in the south of the city, with an average value of 47.73 μ g g⁻¹. Lead levels in subsurface soils ranged from 5.8 μ g g⁻¹ in Hai Al-Swaidi Al-Gharbi to 114.2 μ g g⁻¹ in Hai Al-Naseem Al-Gharbi in the east of the city, with an average value of 24.41 μ g g⁻¹.
- (c) Rural area: Lead levels in surface soils vary from 6.6 μ g g⁻¹ in Hai Dhrat Namar in the west of the city to 72 μ g g⁻¹ in Hai Namar, with an average value of 25.66 μ g g⁻¹. Lead concentration in subsurface soils ranged from 4.0 μ g g⁻¹ in Hai Dhrat Namar to 70.2 μ g g⁻¹ in Hai Namar, with an average value of 20.23 μ g g⁻¹. As shown in Fig. 2, the lead concentration in surface soil samples from the rural area is much lower when compared with that of surface soil samples from the urban habitats. This indicates that lead contamination is entirely due to the burning of the leaded gasoline by automobiles.

Zinc: The zinc content in surface soil samples varies from 4.4 μ g g⁻¹ to 394 μ g g⁻¹, with an average value of 41.60 μ g g⁻¹, whereas subsurface soil samples range from 4.40 μ g g⁻¹ to 210.0 μ g g⁻¹, with an average value of 28.0 μ g g⁻¹. Fig. 2 shows zinc concentration in surface soil samples collected from the urban area to be higher than those from suburban and rural areas, which were attributed to automobile tyres and oil. The spatial variation shows high zinc concentrations associated with the surface soils of the second industrial city compared with the entire city of Riyadh. The exact location of these high levels of zinc in the second industrial city was investigated ¹⁶. Zinc distribution in Riyadh surface soils appeared to be affected by the wind directions in Riyadh city as shown in Fig. 3.

(a) Urban area: The mean zinc concentration in surface soil samples was



Metal variation in surface and subsurface soils with the population density (person/hect-Fig. 2. are) in Riyadh city

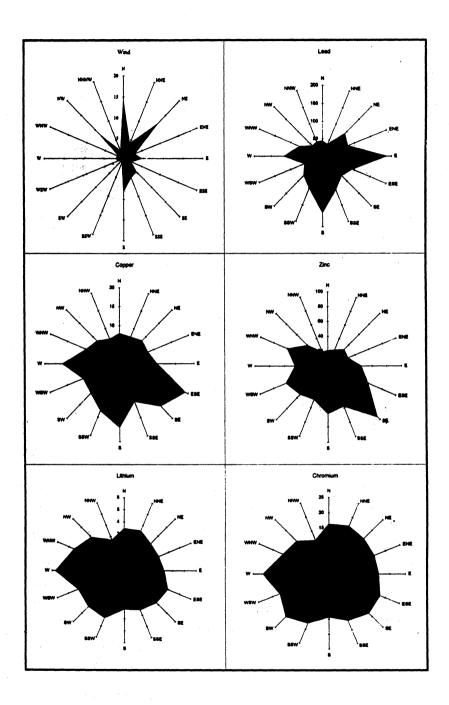


Fig. 3. Metal distribution in surface soil in relation to prevailing winds in Riyadh city

found to be 53.24 µg g⁻¹; the minimum level found in Hai Al-Swaidi was 4.4 μg g⁻¹, and the maximum level at Hai Al-Wazarat was 394 μg g⁻¹. Zinc levels in subsurface soils varied from 5.6 μ g g⁻¹ in Hai Al-Olayah in the north of the city, to 164 µg g⁻¹ in Hai Al-Murabba in the city centre, with an average value of 31.90 $\mu g g^{-1}$.

- (b) Suburban area: An average zinc concentration of 32.34 μg g⁻¹ was found in surface soil samples; the minimum level was 4.4 µg g⁻¹ at Hai Al-Rawabi in the east of the city and the maximum was 286 µg g⁻¹at Hai Al-Azizyah in the south-east of the city. Zinc levels in subsurface soil samples varied from 4.4 µg g⁻¹ at Hai Al-Malik Faisal Quarter in the north-east of the city, to 210 µg g⁻¹ at Hai Al-Hada in the West of the city; the average zinc value was $28.55 \mu g g^{-1}$.
- (c) Rural area: The average level of zinc in surface soil samples was 32.15 ug g⁻¹, which is about the same as in suburban soils, but both are about 40% less than levels in urban area, indicating that automobiles are the main source of zinc. The minimum level was found to be 20 µg g⁻¹ at Hai Dhrat Namar in the west of the city, whereas the maximum was 48 µg g⁻¹ at Hai Namar. Zinc levels in subsurface soils ranged from 11.0 µg g⁻¹ at Hai Dhrat Namar to 44 µg g⁻¹ at Hai Namar, with an average value throughout the area of 23.49 μ g g⁻¹.

Copper: The mean copper content of surface soils was 10.40 µg g⁻¹, with minimum and maximum levels of 2.8 and 72 µg g⁻¹ respectively. In subsurface soils, the mean concentration was 9.0 µg g⁻¹, whereas the minimum and maximum levels were 2.2 and 36.2 µg g⁻¹ respectively. Although Fig. 2 shows close average levels for urban, suburban and rural areas, the spatial variation of copper in surface soils shows relatively high concentrations at the three spots. The first is close to the first industrial city, which might be the reason behind this level; the second is within the city centre, and the third is located in the second industrial city, which was investigated in more detail in Al-Shayeb^{16, 38}. Fig. 3 shows copper distribution in surface soils to be affected by wind directions, but less so than in the cases of lead and zinc distribution.

- (a) Urban area: Copper concentration in surface soils varied from 4.6 μg g⁻¹ at Hai Al-Malaz to 72 μg g⁻¹ at Hai Al-Amal, which is near to the first industrial city and the industrial workshops area, with an average value of 12.06 μg g⁻¹. In subsurface soils copper levels ranged from 3.6 μg g⁻¹ at Hai Al-Malik Fahad Quarter in the north of the city to 25 µg g⁻¹ at Hai Sultanah with an average value of 9.31 μ g g⁻¹.
- (b) Suburban area: The mean copper concentration in surface soils was 9.01 $\mu g \ g^{-1}$, with a minimum level of 2.8 $\mu g \ g^{-1}$ at Hai Al-Tawon in the north of the city and a maximum value of 24.0 µg g⁻¹ at Hai Al-Aziziyah in the south-east of the city. Copper levels in subsurface soils varied from 2.2 µg g⁻¹ at Hai Al-Tawon to 36.2 μ g g⁻¹ at Hai Al-Aziziyah, with an average value of 8.75 μ g g⁻¹.
- (c) Rural area: The copper concentration in surface soils ranged from 8.20 µg g⁻¹ at Hai Dhrat Namar to 13.60 µg g⁻¹ at Hai Namar, with a mean value of 10.73 µg g⁻¹. Copper in subsurface soils varied from 6.0 µg g⁻¹ in Hai Dhrat Namar to 12.0 μ g g⁻¹ at Hai Namar, with an average value of 8.93 μ g g⁻¹.

Nickel, Chromium and Lithium: The mean level of nickel in surface soils

was 42.13 μg g⁻¹; the lowest value of 16.0 μg g⁻¹ came from Hai Al-Swaidi Al-Gharbi in the west of the city and the highest value of 90.2 μg g⁻¹ from Hai Al-Olayah in the north of the city. Nickel concentrations in subsurface soils varied of from 13.20 μg g⁻¹ at Hai Dhrat Namar to 101.2 μg g⁻¹ at Hai Al-Olayah, with an average value of 44.89 μg g⁻¹. The average values of nickel in Riyadh soils is related to population density (Fig. 2).

Chromium content in surface soil samples varied from 6.2 μ g g⁻¹ at Hai Al-Morooj in the north of the city to 45.2 μ g g⁻¹ at Hai Al-Mather in the city centre with a mean value of 16.89 μ g g⁻¹. In subsurface soils, chromium ranged from 5.6 μ g g⁻¹ at Hai Al-Morooj to 47.2 μ g g⁻¹ at Hai Al-Uraijah near the city centre with an average value of 18.29 μ g g⁻¹.

The mean lithium level in surface soils was $3.70 \,\mu g \, g^{-1}$, ranging from $1.4 \, to \, 12.6 \,\mu g \, g^{-1}$. In subsurface soils, lithium varied from $1.2 \, to \, 10.8 \,\mu g \, g^{-1}$ with an average value of $4.0 \,\mu g \, g^{-1}$. Lithium level shows little variation throughout the study area (Fig. 2). However, because it is not related to pollution sources and due to its ubiquitous presence in soils, it was measured to determine metal ratios to trace their natural or man-made sources.

Metal distribution in Riyadh soils: In a large city such as Riyadh, the sources of large-scale pollution are not so much individual emitters as groups of emission sources. The clearest example in our case to a particular source is given by lead, which is primarily emitted by ubiquitous automobiles. The same might be true for zinc (additive in lubricants), which showed high levels along roadsides²⁰ and in industrial locations¹⁶. In these and many other instances there is an overlap between emissions from different sources²¹, which are best described in terms of population density, the size and distribution of refuse incinerators, distribution of industrial activities and motor traffic.

Therefore, in order to estimate the impact of a highway or road network on its neighbourhood environment in Riyadh and to identify the metal levels in urban, suburban and rural habitats it was decided to determine the spatial distribution of metals along a major part of the road network and to discriminate between those pollutants emitted by automobile along such roads and those of industrial origin (another work by Al-Shayeb).

General patterns of metal distribution in Riyadh city

Apart from the road network in Riyadh, there are other pollution sources with a 'spotty' effect leading to large variations in soil heavy metal content over short distances; for example, several metals are released by burning of crude oil in power stations and local sites of metalwork such as garages and of brickworks release high amount of metals into the local environment. Such diffused emissions within the city make the identification of a specific source very difficult. It is generally not possible to do so by direct air sampling methods, as a large number of sites around the suspected source would have to be sampled simultaneously. One approach is to use biological monitoring methods and soil sampling in a form of grid²². Surveys using soils have clearly illustrated the spatial distribution of heavy metal pollution in Riyadh city.

Factors affecting metal distribution in Riyadh city

Lead distribution in Riyadh soils showed spatial variation indicating that their lead content declined progressively from the city centre with a high population density to the rural areas with lesser population density. Much of the city centre had the highest lead levels in soil samples, indicating traffic congestion as the main source of lead. Another possible explanation of this result is that, during the construction of King Fahad Road, which crosses the city centre, all the traffic volume, about 9900 vehicles per hour, were using the small roads and streets within the city centre. This has contributed to an increase in lead contamination within these areas as reflected by the results of the soil survey. These results are in agreement with Everett et al.²³ who found that in areas of high population, lead in plant leaves is higher than that found in less densely populated areas. Similarly, Weis and Barclay²⁴ found the spatial distribution of lead in soils of Essex County, Ontario to be comparable with one showing population centres. In Switzerland, Landolt et al.²¹ found a relationship between the content of lead in spruce needles and population density.

The prevailing wind direction is an important factor in pollutant dispersal. Lead, zinc and to a lesser extent copper distribution in surface soils were affected by the prevailing winds (Fig. 3). Such pollutant distribution 'tails' following the prevailing wind have been reported elsewhere^{25, 26}.

Temperature is likely to influence the pattern of distribution of pollutants through its effects upon air movements. In high temperatures, such as those prevailing in Riyadh, convective air movements will tend to transfer metal particles, especially those of smaller size, upward and away from the site of production. This would cause an increase of deposition on plant leaves and surface soils and also contribute to a rise in background levels in rural areas. The absence of rain will exacerbate this effect, since rainfall provides pollutant scavenging and increases material deposition close to sites of emission.

In addition to the climatic factors, the city topography can affect the spatial distribution of the polluted air. The variations of altitude in Riyadh city shows; the old city centre and areas to the south and south-east of it lie at lower altitudes, which might explain the low levels of metal pollutants found in the west, north and east of the city which lie at higher altitudes.

Finally, the structure of the buildings in the city influences the pattern of pollutant distribution. In the city centre and the commercial area there is a high proportion of high-rise buildings associated with narrow streets which greatly restrict dispersion. Edwards (see Smith²⁷) has suggested that the canyons formed by multiple storey buildings may restrict ventilation and increase the atmospheric lead concentration by several orders of magnitude. In contrast, in the newer areas surrounding the old city the buildings are dominated by villas with only two storeys and broad open roadways. The main motorways are also sited away from residential areas; although these are major sources of metal emission, the impact of this pollution upon the human population, other than those actually using the roadways, is likely to be small.

Comparison of lead content of soils of Riyadh with those from other locations

To put these results of lead surveys in a wider context, comparison with the results of other surveys was thought necessary. A number of surveys of polluted areas have been carried out on the concentration of lead in surface soils. However, the comparison of air pollution in those areas with the pollution in Riyadh by this method alone is difficult.

TABLE-1
METAL VARIATION (µg/g) IN SURFACE AND SUBSURFACE SOILS IN RELATION
TO THE POPULATION DENSITY (PERSONS/HECTARE) IN RIYADH CITY

Ele-	Urban (50- > 200 P/H)		Suburban (0-49 P/H)	Rural (0 P/H)		
ments	Surface	Subsurface	Surface	Subsurface	Surface	Subsurface	
Pb	123.28 ± 17.59	39.56 ± 4.63	47.73 ± 4.63	24.41 ± 1.16	25.66 ± 10.79	20.23 ± 10.78	
Li	3.80 ± 0.14	4.23 ± 0.14	3.59 ± 0.10	3.85 ± 0.12	4.66 ± 0.42	4.23 ± 0.53	
Cu	12.06 ± 0.86	9.31 ± 0.29	9.01 ± 0.27	8.75 ± 0.29	10.73 ± 0.90	8.93 ± 0.91	
Zn	53.24 ± 4.58	31.90 ± 2.04	32.34 ± 2.40	28.55 ± 4.14	32.15 ± 4.68	23.49 ± 4.66	
Cr	16.52 ± 0.44	18.08 ± 0.48	17.06 ± 0.40	18.58 ± 0.52	20.95 ± 1.66	15.59 ± 1.64	
Ni	45.09 ± 1.82	49.42 ± 1.89	40.15 ± 1.79	41.32 ± 2.23	31.85 ± 6.03	33.85 ± 5.61	

Studies of spatial lead distribution in Riyadh soils, provided for the first time, indicate that its mean concentration in surface soils is close to that reported for urban soils from Birmingham, England²⁸, but much lower than those found in Jeddah²⁹ which are about ten times higher (Table-2). In Riyadh surface soils, as expected, the lead concentration is high in areas of high traffic and samples from the city centre have higher concentrations as compared to those of other areas (Fig. 2). In rural areas near to Riyadh, lead levels were similar to those found at rural sites by other researchers. However, lead concentrations in surface soils in these rural areas ranged from 6.6 to 72 µg g⁻¹, with an average of 25 µg g⁻¹, which is higher than the normal lead content in the Scottish soils³⁰, i.e., 20 ug g⁻¹, indicating a wider dispersion of lead under the environmental eircumstances prevailing in Riyadh. Lead pollution in the surface soils along roadsides in Riyadh was higher than that observed by earlier workers²⁰. The high mean lead level of 908 µg g⁻¹ is not unusual bearing in mind the generally high traffic density in Riyadh city, but it is significantly lower than the mean value of 2613 μg g⁻¹ for a motorway in England³¹. An extremely high lead level (6121 μg g⁻¹) in Ring road (east) surface soil samples, which has an average of 2650 µg g⁻¹, was found at its intersection with Makkah road. The mean lead concentration in industrial locations¹⁶ is higher than that of Riyadh's urban areas and other industrial areas reported by other researchers in Table-2. The industrial workshops area has elevated lead levels with a mean value of 1442 µg g⁻¹, which is higher than from roadside soils. The highest lead concentration recorded in any Riyadh surface soils, 9396 µg g⁻¹, was found in this industrial area. It was difficult in

TABLE-2 COMPARISON OF LEAD CONCENTRATIONS IN SOILS OF RIYADH WITH THOSE OF OTHER LOCATIONS

	Conc	centration (µg			
Location	Min Max		Mean	Reference	
Urban					
Birmingham, England	75	350	180*	Davies & Houghton ²⁸	
Ontario, Canada	18	1450	482	Linzon et al.39	
London, England	109	1840	523*	Davies et al.40	
Salamanca, Spain	20.1	92.6	53.1	Sanchez-Camazano et al.	
Baghdad, Iraq	32	950	267	Khalid et al.41	
Giza, Egypt			30	El-Sherif & Hanna ¹¹	
Jeddah, Saudi Arabia	95.7	6082	1343	Zolaly ²⁹	
Riyadh, Saudi Arabia	18.2	1461	123	Present work	
Rural					
Birmingham, England	14	74	42*	Davies & Houghton ²⁸	
London, England	17	67	30*	Davies et al.40	
USA			20	Scanlon ⁴²	
Salamanca, Spain	10.1	26.3	20.4	Sanchez-Camazano et al.	
Mumbai, India			36	Krishnayya & Bedi ⁴³	
Mt Pleasant, USA	100	220	172	Francek ⁴⁴	
Jeddah, Saudi Arabia	25	28.3	26.6	Zolaly ²⁹	
Riyadh, Saudi Arabia	6.6	72	25	Present work	
Roadside					
Guipuzcoa, Spain	49.9	178.9		Garcia & Millan ⁴⁵	
USA			735	Scanlon ⁴²	
Mumbai, India			500	Krishnayya & Bedi ⁴³	
Nigeria '			247	Ndiokwere ⁴⁶	
M4 England			2613	Bevan et al.31	
Mt Pleasant, USA	100	840	320	Francek ⁴⁴	
Jeddah, Saudi Arabia	286	794	541	Zolaly ²⁹	
Riyadh, Saudi Arabia	37.6	6121	908	Al-Shayeb & Seaward ²⁰	
Industrial					
Dublin	39	540		Fleming & Parle ²⁶	
Baghdad, Iraq	32	40	36	Khalid et al.41	
Helwan, Egypt	19	28		El-Sherif & Hana ¹¹	
Armadale, Scotland	5.5	322.2	73.1	Gailey & Lloyd ⁴⁷	
Jeddah, Saudi Arabia			180.7	Zolaly ²⁹	
Yanbu, Saudi Arabia	4.9	79.63		Mashhour ⁴⁸	
Riyadh, Saudi Arabia	28	9396	454	Al-Shayeb ¹⁶	

^{*}EDTA: extractable lead.

this industrial area to discriminate between lead emitted by vehicles and that from industrial activities. When excluding the results of this industrial area and the roadside samples from the Second Industrial City, the mean lead content in surface soils from the industrial locations decreases to 123 $\mu g g^{-1}$, indicating that lead contamination in Riyadh city is mostly due to emissions from leaded gasoline by automobiles.

Surface/subsurface ratios

Table-3 records the ratios of surface mean metal content to mean subsoil content in the studied areas. Lead is markedly enriched in surface soil samples due to general environmental contamination and the arid conditions, particularly along the roadsides where a ratio of 20.38 is attained. This is supported by Chow³² who reported that the lead content of a US highway was as much as 403 μ g g⁻¹ in the top 5 cm layer and decreased to 60 μ g g⁻¹ at 10–15 cm. The most important reason for high differences in these concentrations that lead is not very mobile, mostly accumulating in the top 5 cm of the soil profile³³. The ratio grades from low values in rural areas to higher values in suburban and urban areas, with the highest values from roadsides.

Although zinc has greater mobility than lead²⁵, it similarly shows enrichment in the upper surface soils, which can be attributed to the low precipitation in the study areas. Zinc enrichment in surface soils showed a similar gradient as shown by lead suggesting a common source, but the highest ratio was found in the Second Industrial City indicating an industrial source. Copper enrichment was very obvious in roadside soils. Chromium and nickel show no significant differences between the levels in different layers compared with those at the rural area. Lithium ratios were near unity indicating its soil origin.

These results were confirmed by the results of metal distribution in soil profiles¹⁵. Profile samples show that lead, zinc and copper were largely concentrated in the top 5 cm soil, confirming an airborne origin. It was found that approximately 75% of the lead, 56% of the zinc and 40% of the copper are concentrated in the top 5 cm. Similar findings were reported by other studies^{34–37}. Chromium declined slightly with soil depth, whereas the levels of nickel and lithium did not change with depth, indicating parent material as their origin.

TABLE-3
SURFACE/SUBSURFACE SOILS RATIOS

Location	Pb	Zn	Cu	Cr	Ni	Li
Urban	3.851	2.018	1.413	0.951	0.937	0.950
Suburban	2.090	1.466	1.093	0.971	1.035	1.005
Rural	1.689	1.481	1.233	1.423	0.937	1.185
Roadside ²⁰	20.381	4.132	4.568	1.432	1.063	1.019
Second Indust. City ¹⁶	3.190	4.250	2.220	1.200	1.140	1.110
First Indust. City ¹⁶	3.540	2.920	1.975	1.276	1.109	0.978

Lithium as a reference element: Lithium concentrations in surface and

subsurface soils from different locations in Riyadh city varied within a very narrow range (Table-4).

TABLE-4
LITHIUM LEVELS IN SOIL SAMPLES FROM DIFFERENT
LOCATIONS IN RIYADH CITY

Location	Surface soil			Subsurface soil		
	Min.	Max.	Mean	Min.	Max.	Mean
Urban	1.60	10.20	3.79	1.60	10.80	4.23
Suburban	1.40	12.60	3.59	1.20	9.60	3.85
Rural	3.40	5.99	4.66	2.19	9.40	4.23
Roadside ²⁰	1.40	6.99	3.02	0.80	8.39	3.62
First Industrial City ¹⁶	2.52	5.40	3.46	1.80	6.96	3.90
Second Industrial City ¹⁶	2.40	7.60	4.04	2.60	6.40	3.67
Industrial Area ¹⁶	1.68	3.72	2.33	_		

For the sake of comparison the results of roadside soils²⁰ and industrial location soils 16 were included. Although these locations varied significantly in the pollutant levels, the mean lithium content in surface and subsurface soils is more or less the same. These results are supported by its consistent levels in soil profiles¹⁵, indicating parent material as their origin rather than pollutant sources. Therefore, if the ratios between a certain metal and lithium are consistent at different locations, this might indicate a common source for both elements, whereas, major deviation from the ratio shown in Table-5 might be considered as metal enhancement in the soil. Therefore, from Table-5, lead in surface soils shows to be enhanced in all locations, except the suburban area, which has a mean ratio close to the range of the rural area. Zinc and copper in surface soils showed similar results to those of lead, but to a lesser extent. Only in the Industrial Workshops Area did chromium show enhancement, whereas nickel did not show this in any location, which might indicate a soil origin.

TABLE-5 METAL TO LITHIUM RATIOS IN SOIL SAMPLES FROM DIFFERENT LOCATIONS IN RIYADH CITY, RANGE BETWEEN BRACKETS

Location	Pb	Zn	Cu	Cr	Ni			
(a) Surface soils								
Urban	36.31	15.68	3.48	4.59	11.14			
Suburban	13.85	9.19	2.55	4.86	10.85			
Rural	5.59 [1.50–12.71]	7.05 [4.55–11.25]	2.36 [1.83–3.40]	4.57 [3.83–6.15]	7.14 [3.60–13.94]			
Roadside ²⁰	246.16	24.19	12.56	6.67	7.71			
First Industrial City ¹⁶	70.95	90.59	12.92	6.53	8.24			
Second Industrial City ¹⁶	26.06	39.31	4.71	5.02	6.18			
Industrial Area ¹⁶	668.39	120.60	71.33	10.45	13.51			

Location	Pb	Zn	Cu	Cr	Ni			
(b) Subsurface soils								
Urban	10.39	7.94	2.31	4.59	11.49			
Suburban	6.98	8.13	2.34	5.08	3.40			
Rural	4.72 [1.08–13.00]	5.51 [3.54–8.15]	2.19 [1.63–2.73]	4.19 [2.13–8.27]	8.49 [4.96–15.93]			
Roadside ²⁰	23.75	5.78	2.74	4.52	7.18			
First Industrial City ¹⁶	26.03	45.28	5.89	4.96	7.39			
Second Industrial City ¹⁶	8.97	9.32	2.27	4.62	5.89			

In subsurface soils, lead appeared to be enhanced in roadsides and the First Industrial City. Zinc showed enhancement in the industrial locations. The First Industrial City showed enhanced copper content. The ratios shown by chromium and nickel were within their ranges in the rural area indicating their soil origin rather than pollution sources.

Conclusions

Saudi Arabia's expanding economy in the 1970s together with low petrol prices has led to an increase in car ownership. This coupled with the high lead content of petrol (0.60 g L⁻¹) explain the high levels of pollution in Riyadh environment. In addition, a wide range of industrial activities, represented by the First Industrial City and the Industrial Workshops Area, take place within the city. Due to the above-mentioned pollution and other scattered sources, such as power stations, brickworks and refuse incinerators, it was essential to introduce a suitable monitoring technique by which a baseline data can be obtained and existing sinks and 'hot spots' of pollutant metals identified. The results of an extensive surface soil grid survey revealed that pollution levels changed dramatically over short distances. This indicated the importance of such surveys to give a more realistic picture of pollutant distributions. Soil surveys have illustrated that the main sources of atmospheric metals in Riyadh city were automobile exhaust emissions and industrial activities in the First Industrial City and the Industrial Workshops Area. The results of this survey represents the spatial distribution of lead which showed a gradient declining outwards from the city centre, with metal burdens associated with particular human activities, the deposition influenced by wind and topography. Although airborne metallic fumes and particles could have entered Riyadh from outside sources, since almost all of the lower values were located at the periphery of the city, the effect of external sources does not seem to have been important.

The contamination of Zn, Pb, Cu and, to a lesser extent, Cr were noticed in the top layer of Riyadh soils suggesting that falling dust from polluted air is the reason behind this surface enrichment. This is supported by the results of metal distribution in soils profiles, which show surface enrichment for the studied metals.

Finally, lead will have a relatively high residence time in the warm dry atmosphere of Riyadh and this, coupled with the great mobility of dust, will increase the exposure of human respiratory pathways to metal contamination. On

the other hand, none of the vegetable and fruit products consumed within the city of Riyadh are grown there except the date (fruit), which was not a source of lead if carefully washed before eating³⁸. Therefore, the route of exposure to the metal burden in the Riyadh environment is likely to be through respiration processes rather than food consumption.

ACKNOWLEDGEMENT

We are most grateful to the Saudi Government for financial support of this research programme.

REFERENCES

- 1. K.G. Tiller, Science, 9, 113 (1989).
- 2. B.J. Alloway, Heavy Metals in Soils, John Wiley & Sons, New York (1990).
- 3. H. Kung and M. Ying, Catena, 17, 417 (1990).
- 4. Z. Kafka and M. Kuras, Fresenius Environ. Bull., 3, 407 (1994).
- 5. D. McGrath, Sci. Total Environ., 164, 125 (1995).
- 6. M. Bloemen, B. Markert and H. Lieth, Sci. Total Environ., 166, 137 (1995).
- 7. M. Sanchez-Camazano, M.J. Sanchez-Marin and L.F. Lorenzo, Sci. Total Environ., 146/147, 163 (1994).
- 8. G.T. Goodman and T.M. Robert, *Nature*, **231**, 287 (1971).
- 9. N.F.Y. Tam, W.K. Liu, M.H. Wong and Y.S. Wong, Sci. Total Environ., 59, 325 (1987).
- 10. Y.B. Ho and K.M. Tai, Environ. Pollut., 49, 37 (1988).
- 11. A.F. El-Sherif and F.S. Hanna, Bull. NRC Egypt, 2, 138 (1977).
- 12. M.A. El-Sahaf, M.Sc. Thesis, Physics Department, King Saud University, Riyadh, Saudi Arabia (1983).
- 13. K.O. Ahmed, H.M. Al-Swaidan and B.E. Davies, Sci. Total Environ., 138, 207 (1994).
- 14. M.A. Al-Rajhi. M.R.D. Seaward and A.S. Al-Aamer, Environmenta International, 22, 315 (1996).
- 15. S.M. Al-Shayeb and M.R.D. Seaward, Asian J. Chem., 13, 424 (2001).
- 16. S.M. Al-Shayeb, Asian J. Chem., 14, 1161 (2002).
- 17. S.B. Bradley and J.J. Cox, Sci. Total Environ., 50, 103 (1986).
- 18. A.I. Page and T.J. Ganje, Environ. Sci. Technol., 4, 140 (1970).
- 19. N.I. Ward, in: A.R. Date and A.L. Gray (Eds.), Applications of Inductively Coupled Plasma Mass Spectrometry, Chapman & Hall, New York, pp. 189-219 (1989).
- 20. S.M. Al-Shayeb and M.R.D. Seaward, Asian J. Chem., 13, 407 (2001).
- 21. W. Landolt, M. Guecheva and J.B. Bucher, Environ. Pollut., 56, 155 (1989).
- 22. T.M. Roberts, J. Environ. Planning Pollut. Control, 1, 43 (1972).
- 23. J.L. Everett, C.L. Day and D. Reynolds, Fd. Cosmet. Toxicol., 5, 29 (1967).
- 24. I.M. Weis and G.F. Barclay, J. Great Lakes Res., 11, 339 (1985).
- 25. P. Little and M.H. Martin, Environ. Pollut., 3, 241 (1972).
- 26. G.A. Fleming and P.J. Parle, Ir. J. Agric. Res., 16, 35 (1977).
- 27. W.H. Smith, J. Air Pollut. Control Assoc., 26, 753 (1976).
- 28. B.E. Davies and N.J. Houghton, Urban Ecol., 8, 285 (1984).
- 29. A.M.A. Zolaly, Ph.D. Thesis, University of Sheffield, UK (1987).
- 30. D.J. Swaine and R.L. Mitchell, J. Soil Sci., 11, 347 (1960).

31. D.M. Bevan, D M. Colwill and L.E. Hogbin, TRRL Laboratory Report 626, Crowthorne, Berkshire (1974).

- 32. T.J. Chow, Nature, 225, 295 (1970).
- 33. A. Falahi-Ardakani, Ecotoxicol. Environ. Safety, 8, 152 (1984).
- 34. F. Beavington, Aust. J. Soil. Res., 11, 27 (1973).
- 35. G.K. Rutherford and C. R. Bray, J. Environ. Qual., 8, 219 (1979).
- 36. P.O. Scokart, K. Meeus-Verdinne and R. De Borger, Water Air Soil Pollut., 20, 451 (1983).
- 37. W.A. Glooschenko, L. Holloway and N. Arafat, Aquatic Bot., 25, 179 (1986).
- 38. S.M. Al-Shayeb, Asian J. Chem., 14, 1185 (2002).
- S.N. Linzon, B.L. Chai, P.J. Temple, R.G. Pearson and M.L. Smith, J. Air Pollut. Control Assoc., 26, 650 (1976).
- 40. B.E Davies, D. Conway and S. Holt, J. Agric. Sci., 93, 749 (1979).
- 41. B.Y. Khalid, B.M. Salih and M.W. Issac, Bull. Environ. Contam. Toxicol., 27, 634 (1981).
- 42. P.F. Scanlon, Sci. Total Environ., 59, 317 (1987).
- 43. N.S. Krishnayya and S.J. Bedi, Environ. Pollut. Ser., A40, 221 (1986).
- 44. M.A. Francek, Environ. Pollut., 76, 251 (1992).
- 45. R. Garcia and E. Millan, Sci. Total Environ., 146/147, 157 (1994).
- 46. C.L. Ndiokwere, Environ. Pollut., 7, 35 (1984).
- 47. F.A. Gailey and O.L. Lloyd, Water Air Soil Pollut., 24, 1 (1985).
- 48. A.M. Mashhour. Proceedings of the Industrial Air Pollurion Symposium, 15–17 November, Riyadh, pp 486-491 (1993).

(Received: 25 April 2002; Accepted: 3 February 2003)

AJC-3014

(ICAVS-2)

THE SECOND INTERNATIONAL CONFERENCE ON ADVANCED VIBRATIONAL SPECTROSCOPY

NOTTINGHAM, UK

AUGUST 24-29, 2003

Contact:

http://www.icavs.org