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Metals Content in Soils of the Industrial Cities and the Industrial Workshops Area in Riyadh, Saudi-Arabia

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The metals content (Pb, Zn, Cu, Cr, Ni and Li) of surface and subsurface soils was determined in the first and second industrial cities and the industrial workshops area in Riyadh city. Their levels were investigated in relation to soil depth and the land-use. The levels of Pb, Zn and Cu were found to be elevated in the industrial workshops area and the first industrial city and to a lesser extent in the second industrial city. Lead levels were attributed to the automobile emission whereas Zn and Cu were found to be associated with the industrial activities. Although the second industrial city is newly developed, results of this work have revealed that there are already high Zn, and to a lesser extent Cu, levels at certain locations, where it is recommended that measures to control their release be adopted immediately. Soil profile 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: Metal content, Soils, Industrial cities, Riyadh, Saudi-Arabia

INTRODUCTION

Soil contamination by heavy metals resulting from the emission of fumes and smoke from industrial plants is recognized as a major problem in different countries. Burkitt *et al.*[1] studied the distribution of heavy metals in the vicinity of an industrial complex at Avonmouth. Although there was a rapid fall in lead concentration as distance from the works increased, significant quantities could still be detected about 11 km away. Linzon *et al.*[2] investigated the degree and extent of lead contamination of soils in the vicinity of secondary lead industries in Ontario. The mean lead level of surface soil was 2615 ppm around the secondary smelter and 1996 ppm around the battery manufacturer. Nakos[3] found the levels of Pb and Cd in surface soil samples collected from a site of concentrated industrial development near Athens to be 2–7 and 6–34 times higher than those in similar soil samples from remote (rural) areas. Bunzl *et al.*[4] found Ni concentration in soils around a coal-fired power plant ranged from 5 to 40 $\mu g\ g^{-1}$, which are within the average Ni-content in German soils (range *i.e.* 10–50 $\mu g\ g^{-1}$).

Soils in mine areas often have very high contents of heavy metals. De Nobili *et al.*[5] reported high lead concentrations up to 71,000 μg g^{-1} in the soil of a mine area in S.W. Sardinia. Kung and Ying[6] determined Pb, Zn, Cr, Cd and Hg concentration 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 Kuras[7]. Their results showed that the concentration of heavy metals in some areas was so high that these soils needed immediate decontamination or at least some remedial measures. McGrath[8] 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 top soils of Osnabruck was studied in relation to land use by Bloeman *et al.*[9] The extremely high values around a metal-work 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.

Other studies investigating metal contamination of industrial environments include Warren *et al.*[10], Buchauer[11], Albasel and Cottenie[12], Blake *et al.*[13], Seaward and Mashhhour[14], Hlavay *et al.*[15] and Kovnatsky and Surnin[16].

In Riyadh, there are two industrial cities. The old or first industrial city was established in 1969 and located to the south-east of Riyadh traditional centre (Fig. 1). It is bounded to the east by the freight terminal of the railway station,

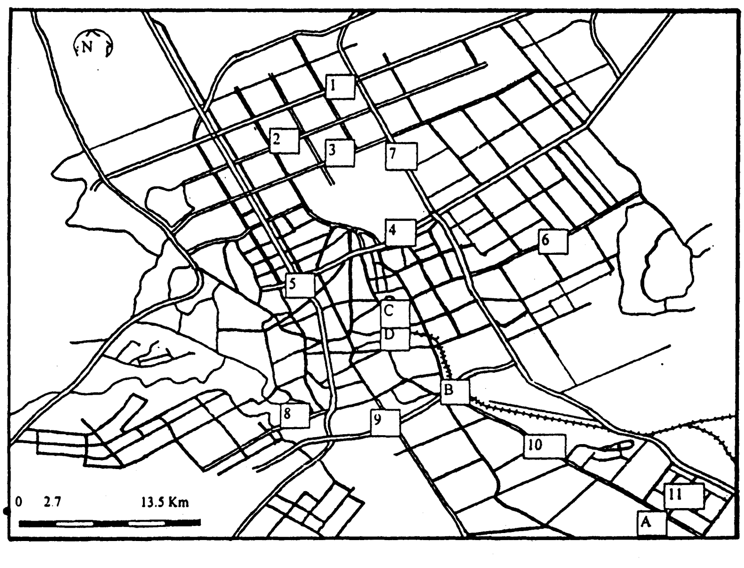

Fig. 1. Riyadh map showing the industrial locations under investigation

1. Ring road (North)
2. A.S.A Mahd road
3. A. Abdullah road
4. Makkah road
5. King Fahad road
6. S.A. Rahman road
7. Ring road (East)
8. Al Swaidi road
9. Ring road (South)
10. Al Kharj road
11. Second industrial city

A. Oil refinery
B. Cement factory
C. First industrial city
D. Industrial area

to the south by an area of industrial workshops, and to the west by Al Kharj road (Fig. 2a). The main reason for choosing the site at that time was the availability of suitable land outside the city, mainly in the south and the east, in addition to the availability of labour and the existence of a good road network. It has an area of 451,028 m^2 and 59 factories.

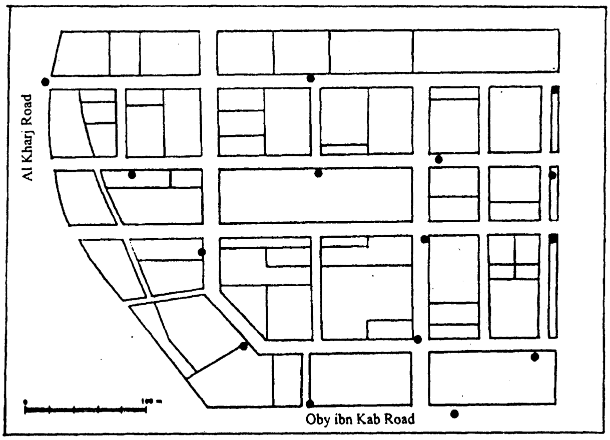

Fig. 2a. Soil sample locations in the first industrial city

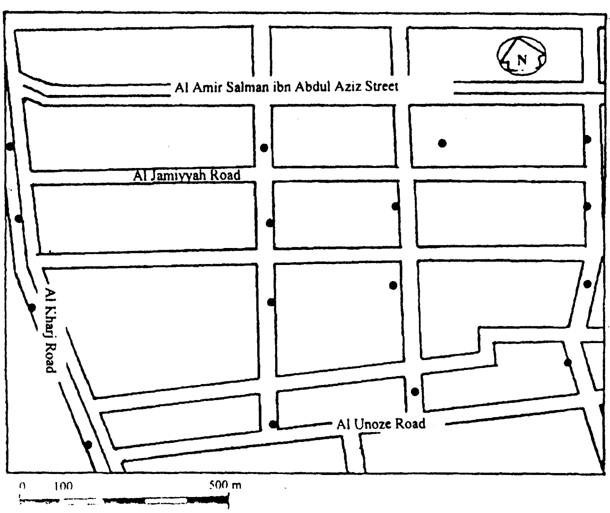

Fig. 2b. Soil sample locations in the industrial workshops area

The construction and growth of the second industrial city resulted from the lack of land space surrounding the first industrial city and from the need for adjacency of industries, which create an ideal opportunity for interaction and integration and for a better industrial environment. It is located on the south-east of Riyadh (Fig. 1), about 18 km from the city centre, and lies between Al-Kharj Road and the Riyadh Ring Road opposite the Riyadh Oil Refinery. It was opened in 1980 and covers an area of 23 million m^2, about 13% of which has been reserved for a residential area for the industrial city. It has 497 factories. The categories of land-use are shown in Table 1. This industrial city has been carefully planned to avoid the shortcomings apparent in the first industrial city. It has larger industrial plots, wider roads and adjacent land spaces for expansion (Fig. 3). It has all utilities, including electricity, water, communication networks, gardens, fire station, bank and clinics.

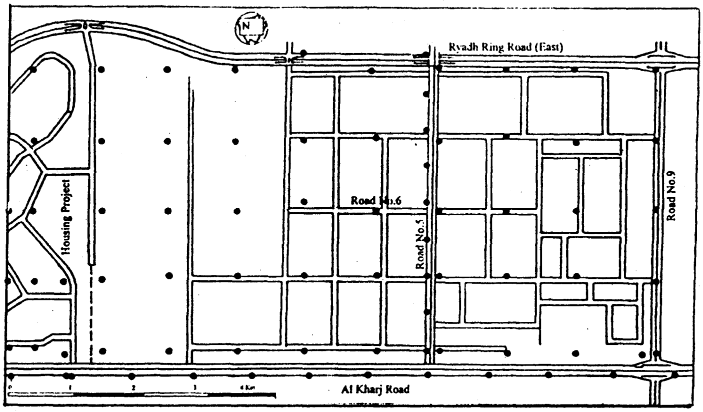

Fig. 3. Soil sample locations in the second industrial city

The environmental pollution has been considered in the establishement of the industrial cities by the employment of modern technology to reduce the emitted pollutants to the minimum. According to government regulations, conditions and guidelines should be met in proposed projects in order to be eligible for the allocation of a plot of land in an industrial city.

TABLE-1
CATEGORIES OF LAND-USE WITHIN THE SECOND INDUSTRIAL CITY

Type	Area × 10^3 m^2	%
Zoned for industrial use	16,000	69.5
Zoned for extension (under development)	4,000	17.5
Area for residential area	3,000	13.0
Total	23,000	100.0

A further industrial area is located to the south-east of Riyadh city centre. It covers an area of about 1,800,000 m^2, and is bounded on the north by the First Industrial City, to the west by Al-Kharj Road, to the south by Al-Unoze Road, and to the east by Al-Kalifa Al-Amin Road (Fig. 2b). This industrial area contains hundreds of privately owned workshops engaged in welding, metalwork, car repairs, painting, etc. Due to the concentration of workshops and narrowness of the local roads, it is subject to very considerable traffic congestion. These highly industrial activities produce large amount of metal pollutants and since most of these workshops involve open-air work, no means have been used to reduce these pollutants. Such pollutants harm workers and affect people in the surrounding areas due to translocation of these pollutants by the winds.

There are very few studies about the metal pollution in the industrial areas in Riyadh city. El-Sahaf[17] has evaluated some atmospheric pollutants in seven places in Riyadh city, among which an industrial area; his findings were 1.93, 1.84, 0.04 and 0.62 ($\mu g\ m^{-3}$) for Pb, Cu, Ni, Zn respectively. Ahmed *et al.*[18] investigated metal concentrations in the dust of Riyadh; the industrial area was among the studied sites. The concentrations of Pb, Cr, Cu and Zn were 305.4, 205.9, 183 4 and 486.8 ($\mu g\ g^{-1}$) respectively. Al-Rajhi *et al.*[19] investigated the concentrations of Cd, Cr, Cu, Ni, Pb, Zn and Li of outdoor and indoor dusts in Riyadh city, the old (Firest) and the second industrial cities were included in their study. They found the old industrial area to contain an appreciable high level of the studied metals in both indoor and outdoor dust.

All the above studies investigated metal pollution in deposited and suspended particulates. But nothing is known about the soil metal levels in the first and the second industrial cities and the workshops area in Riyadh city. This shows the extreme need for this work, which is covering these areas to reveal their metal contents and show their distribution patterns.

EXPERIMENTAL

Sample collection

The first industrial city and the industrial workshops area

These two industrial locations are located within the city of Riyadh and are expected to be hot spots in terms of heavy metal pollution. Thirty surface and subsurface soil samples of the first industrial city and 16 surface soil samples of the industrial workshops area were collected to achieve spatial coverage (Fig. 2a and 2b).

The second industrial city

In order to obtain baseline data for the entire area of the second industrial city and the neighbouring part of the housing project, soil samples were colleced on 1 km × 1 km grid basis (Fig. 3). A total of 156 surface (0–3 cm) and subsurface (5–10 cm) samples were collected using a stainless steel trowel, and placed in 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.

Soil profile sampling

To investigate the origin of the soil metal content in the study area, a total of 40 soil profile samples were collected from the second industrial city. Soil profile samples were collected from five sites at depths of 0–3, 3–5, 5–10, 10–15, 15–20, 20–30, 30–40 and 40–50 cm.

Sample preparation

All samples collected from the field were thinly spread on polyethylene sheets and allowed to dry in air at ambient temperatures. They wre 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 Cox[20] 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 by 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 HNO_3) 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

Metals in the industrial location

The second industrial city

In an effort to establish the distribution and potential hazard of heavy metal levels arising from the second industrial city, and the part reserved as a further residential area, these as well as the industrial area were studied for future monitoring of industrial developments. Apart from a few scattered buildings, the present reserved residential area forms a vast empty area, and is therefore regarded in this study as a buffer zone for the future housing projects. Table-2 summaries the metal content in surface soils of the three areas, and for the sake of comparison the data of the first industrial city and the industrial workshops area are included. The metal content in subsurface soils of the three areas and the first industrial city is summarised in Table-3. Fig. 4 shows the metal contents in surface and subsurface soil samples collected from the second industral city, the buffer zone and the residential complex. In an attempt to identify the industrial origin and sources of the studied metals, the grid survey covering the three areas without the main roads was conducted.

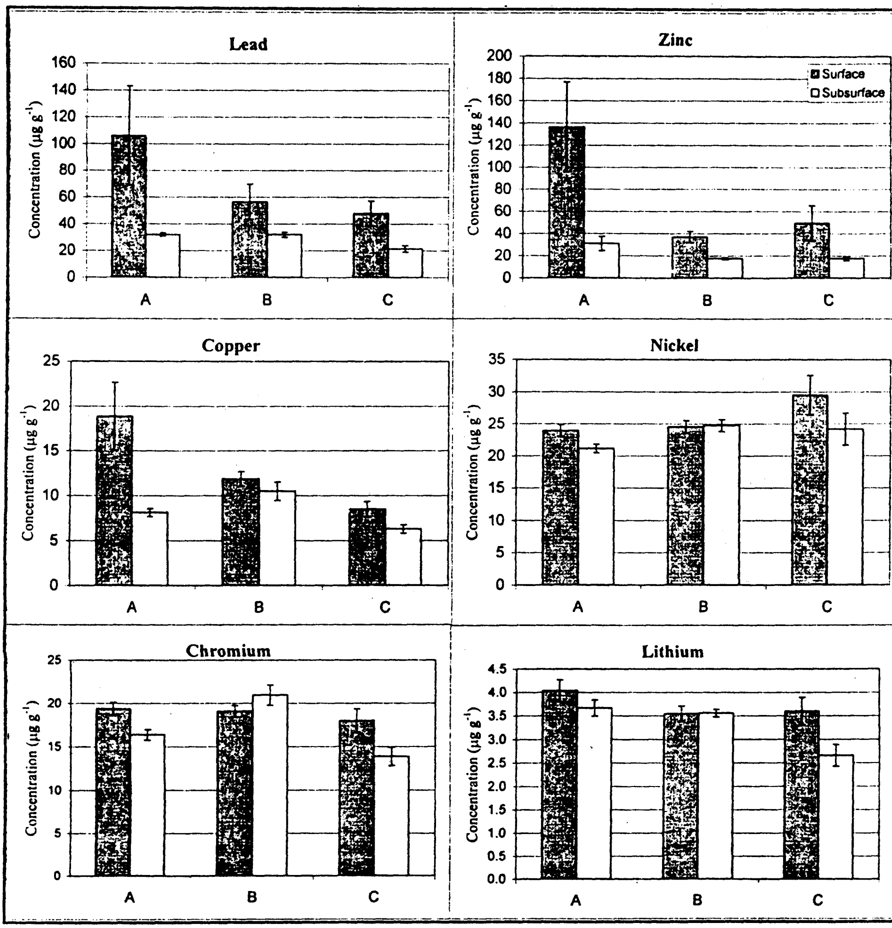

Fig. 4. Metal levels in surface and subsurface soils collected from the second industrial city: (A) Industrial area. (B) Buffer zone (C) Residential complex (mean and SE error bars)

TABLE-2
METAL LEVELS (μg/g) IN SURFACE SOILS FROM INDUSTRIAL LOCATIONS IN RIYADH CITY

Location	Pb	Li	Cu
Second industrial city	106.15 ± 37.06	4.04 ± 0.23	18.88 ± 3.79
Buffer zone	56.67 ± 13.17	3.55 ± 0.16	11.84 ± 0.83
Residential complex	47.92 ± 9.39	3.60 ± 0.29	8.49 ± 0.86
First industrial city	220.53 ± 42.69	3.46 ± 0.22	38.82 ± 11.02
Industrial workshops area	1442.85 ± 549.55	2.33 ± 0.14	160.80 ± 35.59
Rural area	25.66 ± 10.79	4.66 ± 0.42	10.73 ± 0.90

Location	Zn	Cr	Ni
Second industrial city	136.27 ± 40.63	19.40 ± 0.72	23.96 ± 0.91
Buffer zone	37.21 ± 5.16	19.09 ± 0.66	24.57 ± 0.98
Residential complex	118.56 ± 70.55	18.00 ± 1.34	29.48 ± 3.07
First industrial city	317.12 ± 113.04	21.60 ± 1.21	27.66 ± 1.71
Industrial workshops area	277.05 ± 24.05	24.12 ± 2.34	32.00 ± 4.55
Rural area	32.15 ± 4.68	20.95 ± 1.66	31.85 ± 6.03

TABLE-3
METAL LEVELS (μg/g)IN SUBSURFACE SOILS FROM INDUSTRIAL LOCATIONS IN RIYADH CITY

Location	Pb	Li	Cu
Second industrial city	32.00 ± 1.33	3.67 ± 0.17	8.13 ± 0.44
Buffer zone	32.11 ± 1.91	3.56 ± 0.08	10.49 ± 1.02
Residential complex	21.50 ± 2.43	2.66 ± 0.23	6.30 ± 0.48
First industrial city	98.23 ± 28.53	3.90 ± 0.38	22.88 ± 5.03
Rural area	20.23 ± 10.78	4.23 ± 0.53	8.93 ± 0.91

Location	Zn	Cr	Ni
Second industrial city	31.13 ± 6.38	16.41 ± 0.61	21.15 ± 0.68
Buffer zone	17.64 ± 0.85	20.96 ± 1.16	24.77 ± 0.91
Residential complex	17.60 ± 1.90	13.88 ± 1.06	24.18 ± 2.50
First industrial city	170.06 ± 63.39	19.12 ± 1.71	28.65 ± 3.40
Rural area	23.49 ± 4.66	15.59 ± 1.64	33.85 ± 5.61

Lead: The Pb mean content in surface soils in the industrial area was 106.15 μg g^{-1}. The lowest value was 28.20 μg g^{-1}, and the highest was 1008 μg g^{-1} found in Road No. 4 close to a ceramics and a furniture factories. In subsurface soils, the lead content varied from 13.60 to 45.40 μg g^{-1} with an average value of 32.0 μg g^{-1}. The mean Pb content in surface soils in the buffer zone was 56.67

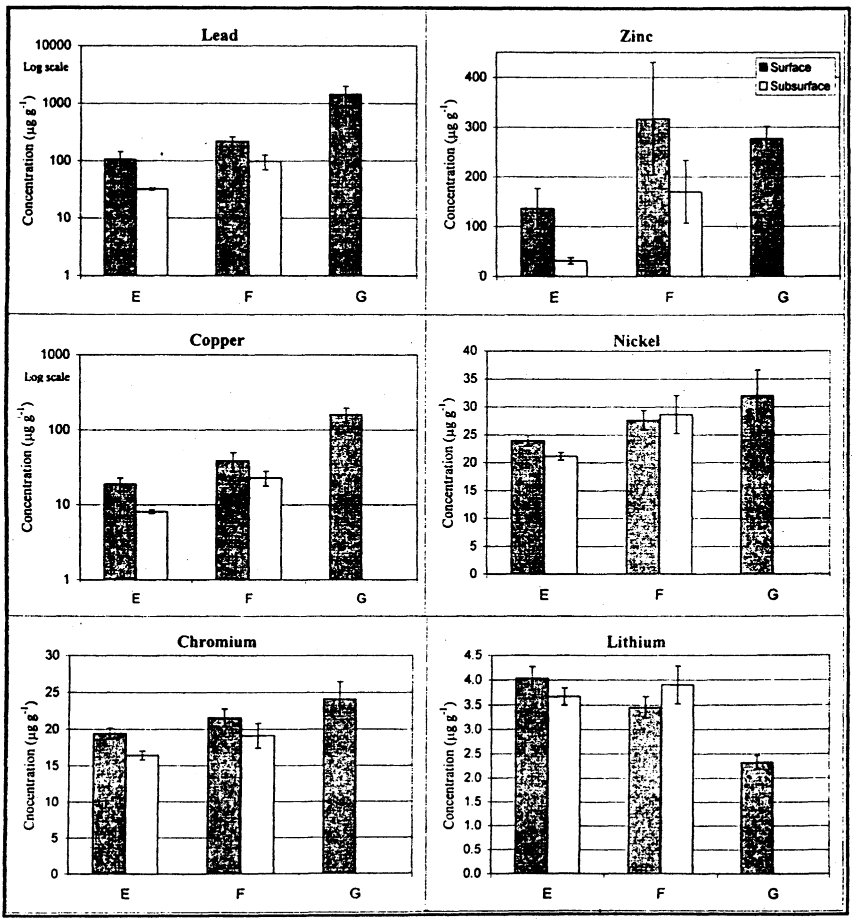

Fig. 5. Metal levels in surface and subsurface soils collected from the second industrial city (E) and the first industrial city (F), and from surface soils from the neighbouring industrial area (G) in Riyadh city (mean and SE error bars)

µg g^{-1}, which is about 47% less than Pb levels in the industrial area. Pb levels in subsurface soils in the buffer zone are very similar to those in the industrial area. The Pb content in the surface soils of the residential complex was 47.92 µg g^{-1}.

Zinc: The Zn content in surface soils was found to be the highest of the metals studied (Fig. 4), with a mean value of 136.27 µg g^{-1}. The minimum Zn concentration in surface soils was 20.60 µg g^{-1}, and the maximum was 1038 µg g^{-1} recorded near a galvanising factory. The next highest level was 460 µg g^{-1} found near another galvanising factory. A level of 288 µg Zn g^{-1} was obtained from the surface soils close to a furniture factory in Road No. 4. Near a factory engaged in cables manufacturing, the Zn concentration in surface soils was 226 µg g^{-1}. The mean Zn content in subsurface soil samples from the second industrial city was 31.13 μg g^{-1} with a minimum level of 12.80 μg g^{-1} and a maximum level of 146 μg g^{-1} recorded near a galvanising factory; the next highest Zn concentration was 120 μg g^{-1} found near a cables factory.

A high Zn value of 216 μg g^{-1} was found in the surface soils of the residential complex which is attributable to the traffic in Al-Kharj Road and to the raw materials used in the building of this complex.

Copper: Surface soils in the second industrial city have higher Cu levels than those of the buffer zone and the residential complex (Fig. 4). The highest Cu level in surface soils was 84.4 μg g^{-1} recorded near a cables factory, and the second highest value was 78.8 μg g^{-1} obtained in the surface soils near another cables factory.

Nickel, chromium and lithium: The content of these elements in surface and subsurface soils did not show large differences between the industrial area, buffer zone and residential complex (Fig. 4).

Roadside Soils in the second industrial city

The metal contents in surface and subsurface soils of the main roads in this industrial city were investigated. These main roads are Al-Kharj Road, Road No. 5 and Road No. 9.

Lead: The mean Pb content in surface soils along the part of Al-Kharj Road bordering this industrial city in the west was 117.49 μg g^{-1}. The highest value was 288.91 μg g^{-1} recorded at the intersection of Road No. 5 with Al-Kharj Road. The Pb content of subsurface soils was 65.02 μg g^{-1}. The Pb content in surface soils along Road No. 9 was 128.04 μg g^{-1} and 24.84 μg g^{-1} in subsurface soils. Along Road No. 5, Pb content in surface soils varied from a minimum of 136.4 μg g^{-1} to a maximum of 1470 μg g^{-1} found at the intersection of Road No. 6 with Road No. 5, near to an iron works factory. The mean Pb content in surface soils along Road No. 5 was 679.04 μg g^{-1}, which is about 6.5 times higher than those in the second industrial city area as a whole. In subsurface soils, the Pb content was 44.86 μg g^{-1}.

Zinc: The Zn content in surface soil samples along Road No. 9 varied from 31.6 to 382 μg g^{-1}. The highest level was recorded at the intersection with Al-Kharj road near a metal works factory. The mean Zn content in surface soil samples was 129.52 μg g^{-1}, and in subsurface soils was 17.48 μg g^{-1}. In surface soil samples along Road No. 5, the Zn content ranged from 58 to 666 μg g^{-1} with an average value of 223.4 μg g^{-1}. The highest Zn level was obtained from the intersection of this road with Road No. 6 near an iron works factory; the mean Zn content in subsurface soils along this road was 18.04 μg g^{-1}.

Copper: The mean Cu content in surface soils along Road No. 9 was 30.0 μg g^{-1}. The maximum Cu concentration was 63.80 μg g^{-1} found near a cables factory. In subsurface soils, the copper content was 8.04 μg g^{-1}. The Cu content in surface soil samples along Road No. 5 varied from a minimum level of 11.8 μg g^{-1} to a maximum of 1166.4 μg g^{-1} recorded at the intersection of this road with Road No. 6, near an iron works factory. The mean Cu contents in surface and subsurface soils were 158.28 μg g^{-1} and 7.8 μg g^{-1} respectively.

Nickel, chromium, lithium: Levels of these elements in surface and subsurface soils of the three roads were comparable with their levels in the industrial area, the buffer zone and the residential complex.

The first industrial city

The metal content in surface and subsurface soil samples from this industrial city is summarised in Tables 2 and 3.

Lead: As shown in Fig. 1, this industrial city is located not far from Riyadh city centre. It is surrounded by a high density road network. Pb distribution in surface soils showed to be associated with traffic on these roads. The Pb level in surface soils varied from 48.96 $\mu g\ g^{-1}$ to a maximum level of 573.60 $\mu g\ g^{-1}$ recorded at Oby ibn Kab Road, which separates this industrial city from its neighbouring industrial area. The next highest level was 549.6 $\mu g\ g^{-1}$ found near a metal smelting factory. Near a spare parts factory 345.6 µg Pb g^{-1} was found in the surface soil. The Pb content in subsurface soils ranged from 16.56 to 364 $\mu g\ g^{-1}$, with an average value of 98.23 $\mu g\ g^{-1}$. The highest level was found at Oby ibn Kab Road, and near a metal smelting factory the Pb level in subsurface soil was 302.4 $\mu g\ g^{-1}$.

Zinc: The mean Zn content in surface soil samples was 317.12 $\mu g\ g^{-1}$, which is more than double that level found in the second industrial city. The highest concentration was 1764 $\mu g\ g^{-1}$ recorded near a paint factory, close to Al-Kharj Road. The next highest concentration was 705.6 $\mu g\ g^{-1}$ found in surface soil located between a furniture factory and a metal plating factory. From surface soils in Oby ibn Kab Road, 513.6 $\mu g\ g^{-1}$ was obtained. Near an aluminium factory, the level in surface soil was found to be 302.4 $\mu g\ g^{-1}$. The lowest Zn concentration was 52.80 $\mu g\ g^{-1}$ found in a garden at the eastern entrance of this industrial city. The Zn content in subsurface soils varied from 24 to 864 $\mu g\ g^{-1}$ with an average value of 170.06 $\mu g\ g^{-1}$. The highest level was found in the same location, where the highest level was also recorded in surface soil samples.

Copper: The Cu content in surface soil samples varied from 11.04 to 182.4 $\mu g\ g^{-1}$, with an average value of 38.82 $\mu g\ g^{-1}$. The highest concentration was recorded at Oby ibn Kab Road; the next highest level of 56.4 $\mu g\ g^{-1}$ was found in surface soil near a metal smelting and forming factory. In subsurface soils, the Cu concentration ranged from 7.80 to 72.00 $\mu g\ g^{-1}$, with a mean value of 22.88; the highest concentration was found in Oby ibn Kab Road.

Nickel, chromium and lithium: The mean Ni level in surface soil was 27.66 $\mu g\ g^{-1}$, ranging from 18.24 to 39.70 $\mu g\ g^{-1}$. In subsurface soils, the nickel level varied from 13.68 to 67.56 $\mu g\ g^{-1}$. The highest value was recorded in Oby ibn Kab Road. The average level of Cr in surface soils was 21.6 $\mu g\ g^{-1}$, ranging from 16.44 to 30.00 $\mu g\ g^{-1}$. Cr level in subsurface soils ranged from 9.36 to 33.24 $\mu g\ g^{-1}$, with an average value of 19.12 $\mu g\ g^{-1}$. The mean Li levels in surface and subsurface soils wre 3.46 and 3.90 $\mu g\ g^{-1}$respectively. The Li content varied from 2.52 to 5.40 $\mu g\ g^{-1}$ in surface soils and from 1.80 to 6.96 $\mu g\ g^{-1}$ in subsurface soils.

The industrial workshops area

This industrial area is located within the city close to the first industrial city to the south. The presence of many car service garages, welding and lathe workshops resulted in high metal concentrations in surface soil samples (Fig. 5). In surface soils, Pb was the highest among the metals investigated, which can be attributed to the large number of congested vehicles, together with the various industrial activities taking place. The mean Pb content was 1442.85 $\mu g\ g^{-1}$, ranging from 153.6 to 9396 $\mu g\ g^{-1}$. This high level was recorded at the western end of Al-Jamiyyah Road.

The mean Zn level in soils was 277.05 $\mu g\ g^{-1}$, ranging from 139.20 to 513.60 $\mu g\ g^{-1}$; the highest level was obtained from Al-Jamiyyah Road. The copper content in surface soils varied from 24 to 520.8 $\mu g\ g^{-1}$, with an average value of 160.80 $\mu g\ g^{-1}$; the maximum level was found in Al-Jamiyyah Road, and the next highest level of 424.8 $\mu g\ g^{-1}$ at Al-Amir Salman ibn Abdul Aziz Street. The mean levels of nickel and chromium were 32.0 and 24.12 $\mu g\ g^{-1}$respectively. The mean Li level was 2.33 $\mu g\ g^{-1}$, ranging from 1.68 to 3.72 $\mu g\ g^{-1}$.

Zinc and copper in the industrial locations

Comparison of the Zn distribution in soils with the land use map shows that the industrial locations are clearly enriched in Zn compared to the rural area. The first industrial city shows the highest mean Zn content in surface soils (317 $\mu g\ g^{-1}$), followed by the industrial workshops area (277 $\mu g\ g^{-1}$) and then the second industrial city with a mean Zn content of 136 $\mu g\ g^{-1}$. The highest zinc concentration in the first industrial city was 1764 $\mu g\ g^{-1}$ found to be close to a paint factory and a roadside. Whereas the highest zinc concentrations within the second industrial city were 1038 and 460 $\mu g\ g^{-1}$found in the vicinity of two sites of galvanising factories.

The industrial workshops areas shows the highest mean copper content in surface soils (160.8 $\mu g\ g^{-1}$), which can be attributed to the metal processing taking place. The first industrial city shows a mean of 38.82 $\mu g\ g^{-1}$ and the highest copper levels were 182.4 and 56.4 $\mu g\ g^{-1}$, which are reported near a roadside and a metal smelting factory respectively. Within the Second Industrial City concentrations of copper in surface soils were found to be higher than those determined from the rural area with a mean value of 18.88 $\mu g\ g^{-1}$. The highest copper levels were 84.4 and 78.8 $\mu g\ g^{-1}$recorded near cables and lighting factories respectively.

Surface/subsurface ratios

Table 4 records the ratios of surface mean metal content to mean subsoil content in the studied areas. Pb is markedly enriched in surface soil samples due to general environmental contamination and the arid conditions, particularly along the roadsides. This is supported by Chow[21] who reported that the lead content of a U.S. highway was as much as 403 $\mu g\ g^{-1}$ in the top 5 cm layer and decreased to 60 $\mu g\ g^{-1}$ at 10–15 cm. The most important reason for high differences in these concentrations that Pb is not very mobile, most accumulating in the top 5 cm of the soil profile[22].

Although Zn has greater mobility than Pb,[23] it similarly shows *enrichment in* the upper surface soils, which can be attributed to the low precipitation in the study areas. Zn and Cu enrichment in surfrace soils was found in the second industrial city indicating an industrial source. Cr and Ni show no significant differences between the levels in different layers. Li ratios were near unity indicating its soil origin.

TABLE-4
SURFACE/SUBSURFACE SOILS RATIOS

Location	Pb	Zn	Cu	Cr	Ni	Li
Second industrial city	3.32	4.38	2.32	1.18	1.13	1.10
Buffer zone	1.76	2.11	1.13	0.91	0.99	1.00
Residential complex	2.23	6.74	1.35	1.30	1.22	1.35
First industrial city	2.24	1.86	1.70	1.13	0.97	0.89
Rural area	1.27	1.37	1.20	1.34	0.94	1.10

These results were confirmed by the results of metal distribution in soil profiles. Profile samples show that Pb, Zn and Cu were largely concentrated in the top 5 cm soil, confirming an airborne origin. It was found that approximately 75% of the Pb 56% of the Zn and 40% of the Cu are concentrated in the top 5 cm. Similar findings were reported by Beavington[24], Czarnowska[25], Rutherford and Bray[26], Scokart *et al.*[27] and Glooschenko *et al.*[28]. Cr declined slightly with soil depth, whereas the levels of Ni and Li did not change with depth, indicating parent material as their origin.

Lithium as a reference element

Lithium concentrations in surface and subsurface soils from different industrial locations in Riyadh city varied within a very narrow range (Table-5). Although these locations varied significantly in the pollutant levels, the mean Li content in surface and subsurface soils is more or less the same. The consistent levels in soil profile, indicating parent material as its origin rather than pollutant sources, support these results. Therefore, if the ratios between a certain metal and Li are consistent at different locations, this might indicate a common source for both elements, whereas, major deviation from the ratio shown in Table-6 might be considered as metal enhancement in the soil. Therefore, from Table-6, Pb in surface soils shows to be enhanced in all locations. Zn and Cu in surface soils showed similar results to those of lead, but to a lesser extent for Cu. Only in the industrial workshops area did Cr and Ni show enhancement, which might indicate a soil origin for both metals in the other studied locations.

In subsurface soils, Pb appeared to be enhanced in the first industrial city (Table-6). Zn showed enhancement in both industrial cities. The first industrial city showed enhanced Cu content. The ratios shown by Cr and Ni were within their ranges in the rural area indicating their soil origin rather than pollution sources.

TABLE-5
LITHIUM LEVLES IN SOIL SAMPLES FROM DIFFERENT RIYADH LOCATIONS

Location	Surface soil			Subsurface soil		
	Min	Max	Mean	Min	Max	Mean
Rural area	3.40	5.99	4.66	2.19	5.40	4.23
Second industrial city	2.40	7.60	0.04	2.60	6.40	3.67
First industrial city	2.52	5.40	3.46	1.80	6.96	3.90
Industrial area	1.68	3.72	2.33	—	—	—

TABLE-6
METAL TO LITHIUM RATIOS IN SOIL SAMPLES FROM DIFFERENT RIYADH LOCATIONS

(a) Surface soils

Location	Pb	Zn	Cu	Cr	Ni
Rural area	5.59	7.05	2.36	4.57	7.14
Second industrial city	26.06	39.31	4.71	5.02	6.18
First industrial city	70.95	90.59	12.92	6.53	8.24
Industrial area	668.39	120.60	71.33	10.45	13.51

(b) Subsurface soils

Location	Pb	Zn	Cu	Cr	Ni
Rural area	4.72	5.51	2.19	4.19	8.49
Second industrial city	8.97	9.32	2.27	4.62	5.89
First industrial city	26.03	45.28	5.89	4.96	7.39

Distribution of elements in soil profiles

The elemental distributions in soil profiles are shown in Fig. 6. Pb, Zn and Cu generally showed highest concentrations in the upper layer of the soil profiles, confirming their airborne origin.

Lead: The distribution of Pb in soil profiles clearly shows that elevated concentrations of Pb are present in surface layers (0–5 cm). The Pb content in the top layer of the soil profiles ranged from 24.58 to 99.38 $\mu g\ g^{-1}$ with an average value of 60.10 $\mu g\ g^{-1}$. At a depth of 12.5 cm, Pb level decreased to 5.0 $\mu g\ g^{-1}$. The relatively high value in the surface layer can be attributed to atmospheric deposition emanating from the combustion of leaded gasoline (*cf.* Beavington[24], Ndiokwere[29], Tam *et al.*[30], Yassoglou[31], Ho & Tai[32]).

Zinc: The variation of Zn levels in soil profiles[23] shows the same trend as in the case of Pb. Although it has greater mobility than Pb, Zn similarly showed enrichment in the upper surface soils, which can be attributed to the low precipitation in the study area. Although, the topsoil layer is enriched with Zn (93.51 $\mu g\ g^{-1}$), it decreased to 16.18 $\mu g\ g^{-1}$ at a depth of 25 cm emphasising its atmospheric origin.

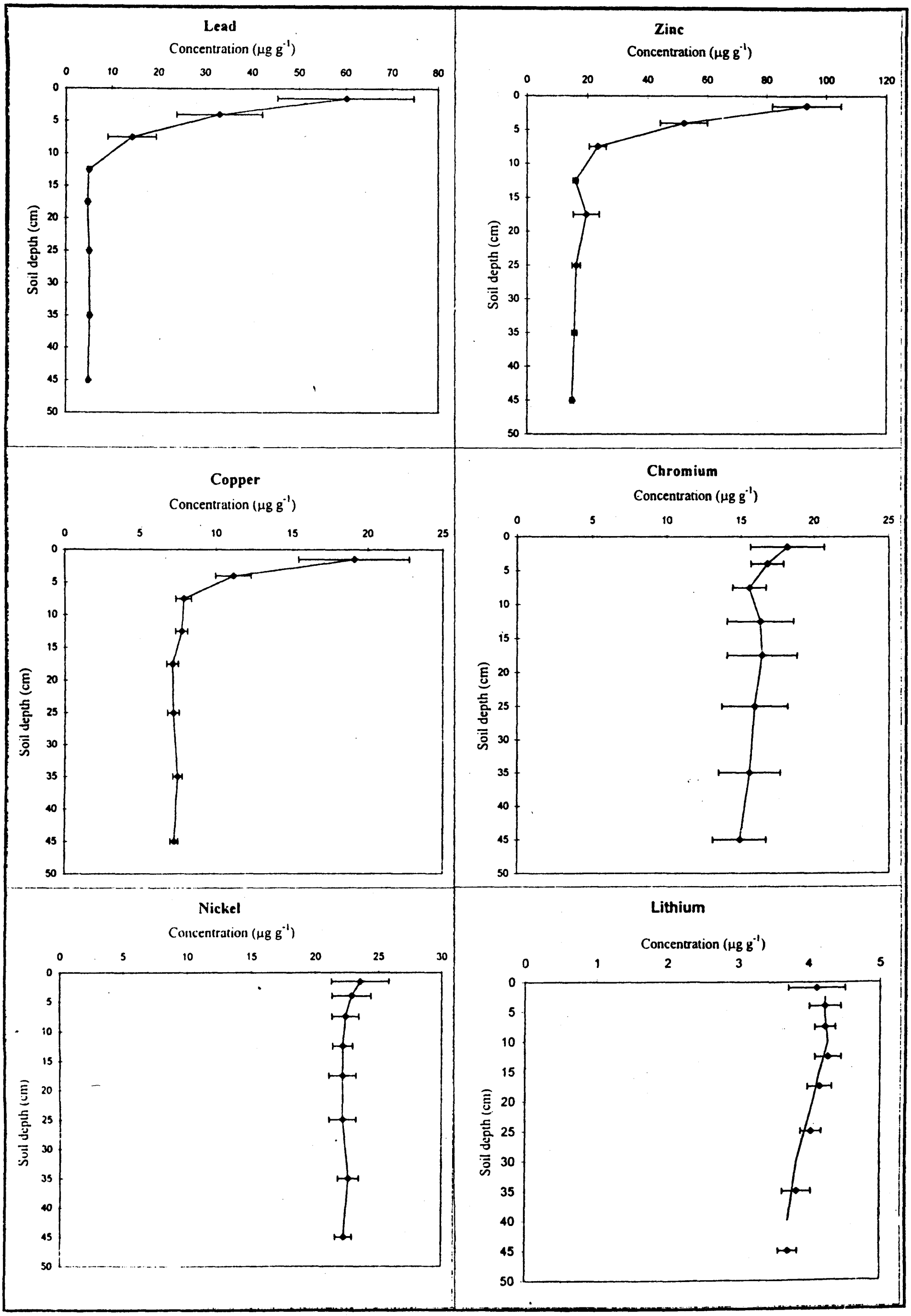

Fig. 6. Metal variation with soil depth in the industrial locations in Riyadh city

Copper: Copper distribution in soil profiles exhibited a pattern similar to that of Zn. The concentration of Cu in the top layer showed relatively surface enrichment, indicating industrial pollution in the top layer with an average of 19.1 $\mu g\ g^{-1}$. At a depth of 25 cm, the Cu level has decreased to 7.23 $\mu g\ g^{-1}$ indicating atmospheric deposition on the surface.

Nickel, chromium and lithium: The vertical distribution of Ni in the soil profiles did not appear to be related to airborne contamination. The Ni content appeared to be mainly related to the texture and the origin of the soil parent materials, and not attributed to sources of pollution. The average concentration in the top layer and at depth 45 cm were 23.54 and 22.26 $\mu g\ g^{-1}$ respectively.

The Cr content in profiles showed slight enrichment in the top layer soils. Cr level in the top layers varied from 25.37 to 10.99 $\mu g\ g^{-1}$, with a mean value of 18.18 $\mu g\ g^{-1}$, and at a depth of 12.5 cm Cr it decreases to 16.34 $\mu g\ g^{-1}$.

Lithium levels in soil profiles showed to be equally distributed. This rather uniform distribution of the element with soil depth confirms that it is not related to any local pollution sources. The Li content in the top layers varied from 5.0 to 2.8 $\mu g\ g^{-1}$, with an average value of 4.12 $\mu g\ g^{-1}$, and at a depth of 25 cm, was 4.04 $\mu g\ g^{-1}$.

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