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Determination of Some Heavy Metals in the Soils of Schools Playground in Riyadh City, Saudi Arabia

قياس لبعض العناصر الثقيلة في تربة ملاعب مدارس مدينة الرياض، المملكة العربية السعودية

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Abstract: The determination of the total content of fifteen elements in soil samples collected from 29 different schools playgrounds in Riyadh metropolitan environment was carried out by inductively coupled plasma mass spectrometry (ICP-MS) combined with microwave digestion technique. According to the results of the concentration at 29 schools' playgrounds in the selected districts, the average concentrations of the heavy metals were determined at 25.91, 29.36, 147.73, 8.02, 17.45, 9.92, 43.72, 2.83, 0.64, 0.5, 0.12, 0.92, 0.45, 27.95, and 1.04 mg/kg (dry soil) for V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Sn, Sb, Pb, and U, respectively. Most school playgrounds with elevated heavy metals concentrations were found in Manfuhah, Al Shifa, Al Yamamah, Sultanah, An Namuthajiyah, Al Wurud and Al Shimaisi residential districts due to their proximity to main traffic roads, industrial areas, and high density residential areas. On the other hand, schools playgrounds with lower heavy metals levels were found in An Nuzhah, Al Aqiq and Al Jazirah residential districts, which may be attributed to less traffic emissions, low residential density, and their distant location from the industrial areas. The measured concentrations levels of the heavy metals in the soil, except for Pb, were below the allowable concentration limits. The Pb concentration exceeded these limits in Manfuhah school playground. The enrichment coefficient values (M_{obs}/M_{crust}) for V, Cr, Mn, Co, Ni, and Cu were less than unity at 0.32, 0.47, 0.25, 0.51, 0.44, and 0.36, respectively, suggesting that the origin of these elements is mostly the local soil. The enrichment coefficient values for Zn and Pb were more than unity at 1.66 and 8.47, respectively, suggesting that these elements are anthropogenic in origin, for example, from the traffic emissions.

Keywords: *Heavy Metals, Soil Contamination, ICP-MS, Schools Playgrounds, Riyadh, Saudi Arabia.*

المستخلص: تضمنت هذه الدراسة تقدير تراكيز خمسة عشر عنصرا ثقيلا في عينات تربة تم جمعها من ملاعب مدارس في أحياء مختلفة في بيئة مدينة الرياض وذلك باستخدام جهاز البلازما مزدوج الحث- مطياف الكتلة مع استخدام تقنية الميكروويف لهضم العينات. كان متوسط تركيز العناصر الثقيلة في عينات التربة التي تم جمعها من ملاعب مدارس في أحياء مختلفة في بيئة مدينة الرياض 25.91، 29.36، 147.73، 8.02، 17.45، 9.92، 43.72، 2.83، 0.64، 0.5، 0.12، 0.92، 0.45، 27.95، 1.04 مليجرام لكل كيلوجرام من التربة الجافة لعناصر الفانيديوم، الكروم، المنجنيز، الكوبالت، النيكل، النحاس، الزنك، الزرنيخ، الموليبدنوم، الفضة، الكادميوم، القصدير، الانتموني، الرصاص، اليورانيوم، على التوالي. ووجد بأن أكثر ملاعب المدارس التي تحتوي على تراكيز عالية من العناصر الثقيلة موجودة في أحياء منفوحة، الشفاء، اليمامة، سلطانة، النموذجية، الورود، الشميسي، بينما وجد أقلها احتواء على هذه العناصر في أحياء النزهة، العقيق، الجزيرة. كان مستوى تراكيز العناصر اقل من الحد المسموح به مقارنة بدراسات سابقة، ما عدا عنصر الرصاص في حي منفوحة. وبحساب قيم معامل التخصيب وجد بانها اقل من الوحدة لعناصر الفانيديوم، الكروم، المنجنيز، الكوبالت، النيكل، النحاس، مما يدل على ان المصدر الأساسي لهذه العناصر هو التربة الأصلية، بينما وجدت قيم هذا المعامل أعلى من الوحدة لعنصري الزنك والرصاص، مما يدل على وجود مصادر أخرى لهذين العنصرين غير التربة، كالإنبعاثات الغازية من عوادم السيارات أو من أجزاء السيارات.

كلمات مدخلية : *عناصر ثقيلة، تلوث التربة، جهاز البلازما مزدوج الحث- مطياف الكتلة، ملاعب مدارس، مدينة الرياض، المملكة العربية السعودية.*

Introduction

Metal pollution of the natural environment is a serious global concern because of the harmful effects of these non-degradable chemicals on biota and human health. Toxic metals (e.g., Lead, Cadmium, Copper, Arsenic, ...) exist in the environment at very low concentrations and can create toxic effects in living systems, even at trace levels (Misra and Mani, 1991). In recent years, many natural elemental concentrations have changed considerably over the whole of the earth's surface as a result of commercial exploitation, agricultural practices, industrial processing, and ultimately, through the disposal of vast quantities of chemical, industrial, and domestic wastes (Martin and Coughtrey, 1982). Lead, Cadmium, Iron, Copper, Manganese, Zinc, and other heavy metals are used as representative trace metals whose levels in the environment represent a reliable indictor for environmental pollution. The exposure of human body to toxic elements such as lead can occur via various routes. For instance, it has been noted that children could ingest toxic metals including dusts via their hands or mouths (Schroeder, 1973). Many studies claimed that for children in urban surroundings, the dust of streets and playgrounds is a potentially significant source of Lead (Hamamci *et al.*, 1997; Sezgin *et al.*, 2003). Therefore, the determination of toxic/heavy metals in soil samples is very important in monitoring environmental pollution (Tüzen, 2003).

Since the early 1980s, Riyadh City, the Capital of Saudi Arabia, has been experiencing an accelerated development and increase in population and urbanization, accompanied by an increase in industrial activities and transportation. The population of the city escalated from 1.4 million in 1986 to more than 3 millions in 1996, and it is currently (2007) estimated at 6 millions (High commission for the development of ArRiyadh, 2006). These large growth rates present immense challenges in the development and planning of the city, and are expected to be associated with increasing air and soil pollutants emissions from various sources, the most important are the industrial and transportation activities. This is indicated by some visible phenomena like the black cloud over some parts in Riyadh City from time to time (Arriyadh Development Authority, 1995).

In this study, the total content of the heavy metals of As, Cd, Cr, Cu, Pb, Ni, Ag, Zn, Mn, V, Sn, Co, Sb, U, and Mo in soil samples collected from different school playgrounds of Riyadh metropolitan area were determined. The measured concentrations of these elements are analyzed and discussed with respect to the location of the playground and maximum allowable limits of the element.

Experimental

1. Samples Collection

Twenty nine soil samples were collected during the months of August and September, 2004, from different schools' playgrounds in the Riyadh metropolitan area. The playgrounds were selected from districts located in the center of the metropolitan area and its peripherals, with considerations to traffic intensity and distance from pollution sources (Figure 1). The choice of sampling point was based on the possibility of collecting samples of relatively undisturbed areas. For each of the twenty nine samples, one kg of top soil samples located between 0 and 20 cm below the surface, were collected and stored in a polyethylene bag using a plastic shovel to avoid any cross contamination. Each top soil sample was a composite of five sub-samples from the four corners and centre of each selected twenty nine playgrounds. The soil samples were air-dried, passed through a 0.5 mm screen to remove rocks and other large particles before analysis, and then sieved to 250 μm. The soil samples were homogenized by quartering, and about 2 g were then stored in plastic bottles inside desiccators at room temperature. Table 1 displays the physical characteristics of the collected soil samples and their measured pH. The pH was determined by a pH meter using a ratio of 1:1 (soil:water), while the grain size analysis was determined by the suspension method, according to Ryan *et al.* (2001).

2. Instrumentation

Interest in inductively coupled plasma mass spectrometry (ICP-MS) analysis has been increasing due to its mutli-element capability and

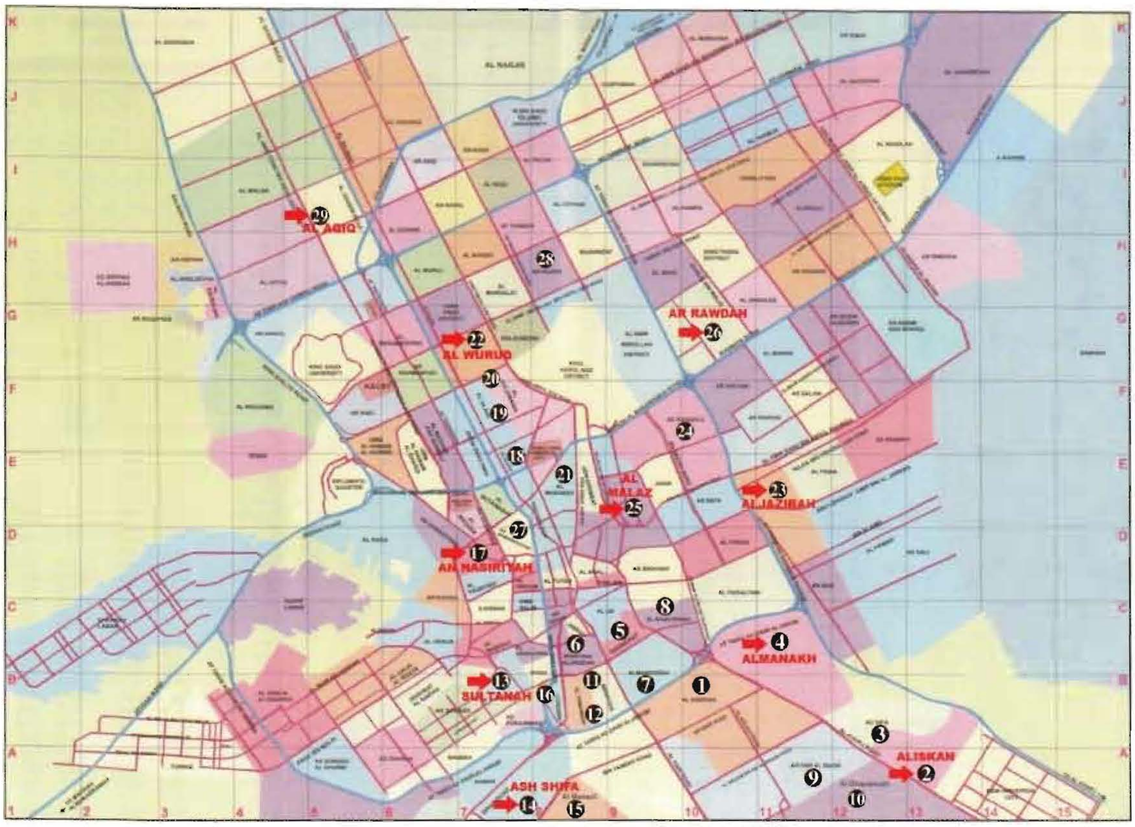

Fig. 1. Location of sampling points in Riyadh City.

Table 1. Grain size analysis and pH of the collected soil samples.

Playground No	Sampling site	pH	Clay %	Silt %	Sand %	Texture Class
1	Al Aziziyah	9.53	10.28	3	86.72	Loamy sand
2	Al Iskan 2	7.64	9.28	2	88.72	Loamy sand
3	Al Iskan 1	7.65	8.28	5	86.72	Loamy sand
4	Al Manakh	8.04	8.28	1	90.72	Sand
5	Ghubaira	7.24	9.28	0	90.72	Sand
6	Manfuhah	7.47	16.28	19	64.72	Sandy loam
7	Al Mansurah	7.69	10.28	0	89.72	Loamy sand
8	Al Khalidiyah	7.62	9.28	1	89.72	Sand
9	Ad Dar Al Baida	7.96	6.28	3	90.72	Sand
10	Al Ghanamiah	7.86	7.28	1	91.72	Sand
11	Old Manfuhah	6.94	14.48	2	83.52	Sandy loam
12	Al Yamamah	7.25	17.48	6	76.52	Sandy loam
13	Sultanah	7.43	14.48	2	83.52	Sandy loam
14	Al Shifa	7.57	16.48	0	83.52	Sandy loam
15	Al Masani`	7.55	13.48	5	81.52	Sandy loam
16	Utaiqah	7.83	9.48	1	89.52	Loamy sand
17	Al Shimaisi	7.66	15.68	2.8	81.52	Sandy loam
18	Al `Ulayya	7.9	10.48	1	88.52	Loamy sand
19	Al `Ulayya	7.8	9.48	5	85.52	Loamy sand
20	Al Sulaymaniyah	7.95	15.48	3	81.52	Sandy loam
21	Al Murabba`	6.85	10.68	2	87.32	Loamy sand
22	Al Wurud	7.06	14.68	3	82.32	Sandy loam
23	Al Jazirah	7.72	9.68	2	88.32	Loamy sand
24	Ar Rabwah	7.96	10.68	3	86.32	Loamy sand
25	Al Malaz	7.29	19.68	10	70.32	Sandy loam
26	Ar Rawdah	8.05	9.68	1	89.32	Loamy sand
27	An Namuthajiyah	7.5	23.68	16	60.32	Sandy clay loam
28	An Nuzhah	7.85	7.68	2	90.32	Sand
29	Al `Aqiq	7.77	5.68	2	92.32	Sand

its ability to secure such analytical task with good reproducibility, low detection limits, extended dynamic range and adequate speed of analysis (Holland and Eaton, 1991). The analytical determination of the studied metals was carried out by ICP-MS: ELAN 9000 (PerkinElmer SCIEX Instruments, Concord, Ontario, Canada) equipped with a peristaltic pump used for sample introduction and auto-sampler model AS 90 from Perkin Elmer used for auto sample transport. Samples were nebulized using a PE cross flow nebulizer. A Pentium digital computer was used to control the instrument and data acquisition, manipulation and storage.

A Milestone ETHOS 1600 advanced microwave digestion system with Rotor MD 1000/6 was used to digest the soil samples. The maximum microwave power is 1600 W. The magnetron mounted in the microwave oven operates at a frequency of 2450 MHz. A six-position rotor (MD 1000/6) was placed in the oven with a rotor speed of 5 rpm. A solution having Mg, Rh, In, Pb and U (for most applications these elements are selected because of covering the whole range of masses) at 10 $ng.g^{-1}$ was used to optimize the instrument in terms of sensitivity, resolution and mass calibration. The $^{140}Ce^{16}O$:^{140}Ce ratio was used to check the level of oxide ions in the plasma that could interfere in the determination of some elements. Furthermore, the level of doubly charged ion was monitored by means of the signal $^{137}Ba^{++}$:^{137}Ba as some instrumental parameters, such as RF power, carrier gas flow and sampling depth, can influence the level of these two ratios. Table 2 illustrates the operating conditions and specifications of the instrument used in this study.

Table 2. Operating conditions of ELAN 9000 ICP-MS.

Parameter	Specification
RF Power	1250 W
Nebulizer gas flow	0.92 L/min
Lens voltage	9.25 V
Analog stage voltage	-1762.50 V
Pulse stage voltage	1050.00 V
Number of replicates	5
Readings/Replicates	1
Sweeps/Readings	30
Scan Mode	Peak Hopping
Dwell Time	40.0 ms
Integration	1200 ms
Internal standard	Rhodium (^{103}Rh)

3. Certified reference material, IAEA SOIL-7

The accuracy and the precision of the analytical method applied for the multi-element determination of soil samples were evaluated by the analysis of a Certified Reference Material (CRM), namely IAEA SOIL-7, obtained from the International Atomic Energy Agency (IAEA), Vienna, Austria.

4. Reagents

Reagents used in the analysis were: Nitric acid (69% v/v), Super Purity grade from Romil, England; Hydrochloric acid (37% v/v) and hydrofluoric acid (40% v/v) were super pure reagents from Merck, Germany; Double de-ionized water (DDW) with specific resistively 18 $M\Omega.cm^{-1}$ was obtained from a Millipore Milli-Q water purification system was used throughout the work; and Rhodium single element 1000 mg/L in 10% (v/v) HCl certified standard from PerkinElmer, USA was used as an internal standard. All the plastic and glassware were cleaned by soaking in dilute HNO_3 and were rinsed with de ionized water prior to use.

5. Calibration

The ICP-MS calibration was carried out by external calibration with the blank solution and three working standard solutions (10, 50 and 100 arts per billion (ppb)), starting from a 10 mg/L multi-element standard solution for ICP-MS (PE Pure, Perkin Elmer) for the elements: Ag, As, Cd, Co, Cr, Cu, Mn, Ni, Pd, V, U and Zn in 5% (v/v) HNO_3, and starting from a 1000 mg/L single standard solutions for ICP-MS (ARISTAR grade, BDH Laboratory supplies, England) for the elements: Mo, Sb and Sn in 5% (v/v) HNO_3.

6. Microwave digestion procedure

Samples were prepared by accurately weighing 200 mg of dried soil samples into a dry and clean TEFLON digestion vessel. Amounts of 5 mL of HNO_3, 1 mL of HCl and 2 mL of HF were added then vessels were sealed and tightened using a torque wrench prior to the digestion and transferred to the microwave oven. Samples were digested inside a microwave oven (Milestone ETHOS 1600) following a digestion program developed to give quantitative recoveries for the elements of interest. Samples were prepared in a batch of six including one reagent blank containing the acid mixture of (HNO_3/ HCl/ HF). After cooling down to ambient temperature, the cap was removed from the vessel and rinsed with distilled deionized water (DDW). The mixture was heated on the hotplate at temperature 120°C for 30 minutes to drive off HF and HCl. The resulting digest was transferred to a 50 ml plastic tube and made up to the mark using deionized water. Solutions were diluted ten times by taking 1 mL into 15 mL plastic tube and a 10 μL from 10 parts per million (ppm) Rhodium (^{103}Rh) standard was added as internal standard, and made up to 10 mL mark with 1% HNO_3.

Some preliminary experiments were carried out in order to evaluate the accuracy of the microwave dissolution scheme as well as the capabilities of ICP-MS measurement. The standard reference material (IAEA SOIL-7) provided by IAEA was analyzed by the applied ICP-MS method, and the obtained analytical results were compared with the certified values; subsequent statistical tests such as F-test and t-test showed that there was no significant differences between the obtained and the certified results (Alotaibi *et al.*, 2006).

Results and Discussion

The concentrations of V, Cr, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Cd, Sn, Sb, Pb, and U determined in the soil samples collected from the twenty nine schools' playgrounds are given in Table 3. The reported results are based on five replicates of the analytical measurements. The analytical results indicated that there are noticeable differences in the concentration of the analyzed elements among the selected playground soils; these differences may be related to various factors such as the type of the soil texture and its origin, the location of the playground in terms of its proximity to high traffic emissions, high density population areas, and industrial areas.

In general, heavy metals cations are most mobile under acid conditions and increasing the pH by liming usually reduces their bioavailability (Alloway, 1995). As the samples were collected from top neutral and alkaline soil, it was observed that the highest accumulated concentrations for the heavy metals of Pb, V, Cr, Cu and Ni were associated with pH values in the range of 7.1-7.7 (Figure 2). Moreover, the soil textural class is dependent on the percentages of clay, silt and sand-sized particles. The clay minerals contribution to soil chemical properties results from their comparatively large surface area and the permanent negative charge of their surface (Alloway, 1995). In general, it was observed that these heavy metals concentrations (i.e., Pb, V, Cr, Cu and Ni) increase with sandy loam soil texture, which contains more clay minerals content compared to other soil texture classes (Figure 3).

The following is an analysis and discussion on some selected heavy metals that were measured at high concentrations. In this discussion, the maximum concentration levels of heavy metals measured in this study are compared with the maximum allowable limits reported in the literature (Sezgin *et al.*, 2003), as presented in Table 4.

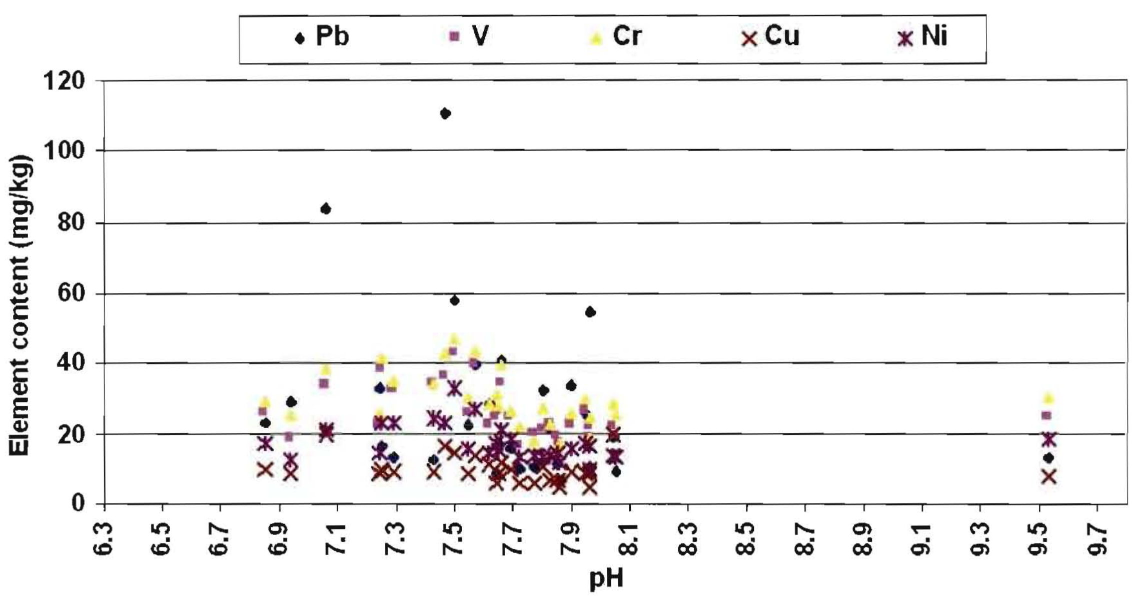

Fig. 2. Heavy metals content vs. pH.

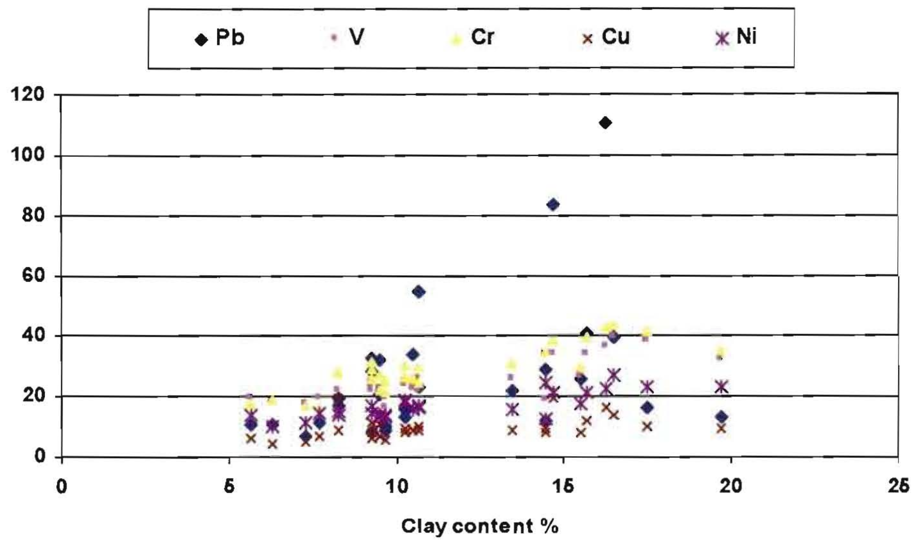

Fig. 3. Heavy metals content vs. clay content.

Lead (Pb)**:** measured Pb concentrations were found to be in the range of 6.90 to 110.51 mg/kg in dry soil samples, with an average concentration of 27.95 mg/kg dry soil. The highest Pb concentration (110.51 mg/kg dry soil) is about five times higher than the maximum concentration (20 mg/kg dry soil) found in typical soils, and is above the acceptable limit of 100 mg/kg dry soil (Sezgin *et al.*, 2003). The highest Pb concentrations in soil samples have been found at schools playground in Manfuhah (110.51 mg/kg dry soil), Al Wurud (83.82 mg/kg dry soil), An Namuthajiyah (58.24 mg/kg dry soil), Ar Rabwah (54.64 mg/kg dry soil), Al Shimaisi (40.69 mg/kg dry soil) and Al Shifa (39.68 mg/kg dry soil). This is due to the fact that Manfuhah's school playground is very close to Al Batha Road (i.e., high traffic emissions), as well as high residential density. In addition, the soil texture of these schools playgrounds is sandy loam (16.28% clay), which increases the soil ability to absorb more concentration of Pb (Alloway, 1995).

Al Wurud's school playground is located on King Fahad Road, where heavy traffic density exists, and is surrounded by high rising buildings resulting in low wind speed at this point, and therefore, Pb and other particulates emitted are unable to diffuse over wide angles. Furthermore, the soil texture of this school playground is sandy loam (14.68% clay). An Namuthajiyah district is located in the center of the city and at less than 500 m from King Fahad Road, which has high traffic density and emissions. Moreover, the soil texture class of this school playground is sandy clay loam (23.68% clay). Ar Rabwah's playground is located on the main Road of Omar Ibn Abdulaziz, where heavy traffic density exists and is about 1 km from the Eastern Ring Road. Al Shimaisi's school playground is on Al Imam Abdul Aziz Mohammed Ibn Saud road, where heavy traffic density exists and the playground is surrounded by high rising buildings and have high residential density. In addition, the soil texture of the playground is sandy loam (15.68% clay). Al Shifa's playground is about 0.5 km away from Dirab Road, with small and medium industrial facilities surroundings (e.g., automotive repair workshops), as well as heavier traffic than other sampling points.

Zinc (Zn): measured Zn concentrations were found to be in the range of 6.54 to 115.84 mg/kg in dry soil samples, with an average concentration of 43.72 mg/kg dry soil. The highest concentration (115.84 mg/kg dry soil) is about two times higher than maximum zinc concentration (50 mg/kg dry soil) found in typical soils, but about two times lower than acceptable and allowable limits (300 mg/kg dry soil). The highest Zn concentrations were found at schools playgrounds in Manfuhah (115.84 mg/kg dry soil), Al Khalidiyah (90.42 mg/kg dry soil), and An Namuthajiyah (90.17 mg/kg dry soil).

Al Khalidiyah's school playground is 500 m away from Southern Ring Road, where very heavy traffic density exists, and is about 1 km away from

Table 3. Heavy metals concentrations in collected soil samples*.

District	Concentration (mg/kg dry soil)*							
	Pb	Cu	Mn	Zn	Cd	Ni	V	Cr
Al Aziziyah	13.48 ±0.12	7.87 ±0.28	149.7 ±1.96	40.69 ±1.10	0.094 ±0.01	18.64 ±0.90	24.08 ±0.60	30.33 ±0.43
Al Iskan 2	8.26 ±0.04	6.02 ±0.21	125.7 ±0.54	24.49 ±1.34	0.082 ±0.01	17.11 ±0.28	24.32 ±0.57	31.15 ±0.40
Al Iskan 1	17.12 ±0.16	8.64 ±0.37	153.2 ±2.81	33.36 ±1.49	0.13 ±0.01	14.85 ±0.17	26.13 ±0.67	27.76 ±0.72
Al Manakh	19.23 ±0.11	19.78 ±0.69	148.6 ±0.29	52.5 ±2.19	0.137 ±0.00	14.02 ±0.16	22.07 ±0.68	28.21 ±0.67
Ghubaira	32.76 ±0.96	8.42 ±0.16	126 ±3.30	60.7 ±1.14	0.174 ±0.00	14.58 ±0.53	22.31 ±0.42	25.97 ±0.72
Manfuhah	110.51 ±0.61	16.37 ±0.54	207.2 ±3.21	115.84 ±3.43	0.238 ±0.01	22.88 ±0.99	36.49 ±1.03	42.81 ±0.79
Al Mansurah	15.73 ±0.42	9.58 ±0.10	142.7 ±3.75	37.2 ±0.82	0.095 ±0.02	18.36 ±0.59	24.56 ±0.32	26.66 ±0.64
Al Khalidiyah	28.18 ±0.60	11.33 ±0.20	122.9 ±1.06	90.42 ±2.13	0.136 ±0.01	14.45 ±0.34	22.21 ±1.15	28.68 ±0.95
Ad Dar Al Baida	10.81 ±0.13	4.29 ±0.23	109.5 ±0.84	23.95 ±4.68	0.068 ±0.01	10.03 ±0.35	18.28 ±0.57	18.66 ±0.73
Al Ghanamiah	6.90 ±0.05	4.74 ±0.16	103.1 ±1.57	16.51 ±0.06	0.055 ±0.01	11.58 ±0.43	17.29 ±0.41	17.20 ±0.35
Old Manfuhah	29.14 ±0.19	8.25 ±0.28	119.7 ±0.39	60.87 ±1.12	0.147 ±0.01	12.32 ±0.22	18.65 ±0.59	25.04 ±0.62
Al Yamamah	16.62 ±0.39	9.84 ±0.40	222.2 ±0.95	31.93 ±1.45	0.132 ±0.01	23.12 ±0.76	38.29 ±1.27	41.78 ±0.76
Sultanah	12.22 ±0.13	9.23 ±0.31	201.8 ±2.27	27.94 ±0.54	0.112 ±0.01	24.51 ±0.97	34.2 ±0.70	34.29 ±0.78
Al Shifa	39.68 ±0.59	13.65 ±0.24	228 ±2.82	67.92 ±1.05	0.188 ±0.01	26.91 ±0.77	39.67 ±0.91	43.54 ±0.33
Al Masani`	22.18 ±0.34	8.7 ±0.25	156.3 ±1.66	51.88 ±0.50	0.114 ±0.01	15.53 ±0.64	25.72 ±0.91	30.65 ±0.60
Utaiqah	21.02 ±0.56	6.64 ±0.26	139.4 ±1.48	28.31 ±0.36	0.086 ±0.01	13.64 ±0.81	22.6 ±0.73	22.19 ±0.31
Al Shimaisi	40.69 ±1.31	11.91 ±0.17	185.8 ±3.09	66.53 ±1.08	0.185 ±0.01	21.15 ±0.50	34.03 ±0.92	39.6 ±0.99
Al `Ulayya	33.82 ±0.43	8.91 ±0.51	122.2 ±1.60	41.26 ±1.35	0.088 ±0.01	15.57 ±0.31	22.37 ±1.16	25.9 ±0.74
Al `Ulayya	32.17 ±0.57	10.83 ±0.10	114.5 ±1.38	50.76 ±1.13	0.107 ±0.01	13.32 ±0.39	20.82 ±0.48	27.00 ±0.79
Al Sulaymaniyah	25.67 ±0.21	8.32 ±0.26	139.2 ±0.61	17.01 ±1.30	0.097 ±0.01	17.39 ±0.79	26.67 ±1.38	29.73 ±1.33
Al Murabba`	23.00 ±0.54	10.02 ±0.26	161 ±1.63	53.69 ±0.96	0.166 ±0.01	16.83 ±0.18	26.02 ±1.12	29.22 ±1.03
Al Wurud	83.82 ±0.32	19.56 ±0.42	190 ±3.78	53.43 ±1.12	0.348 ±0.02	21.13 ±0.07	33.73 ±0.90	38.08 ±0.96
Al Jazirah	10.17 ±0.11	5.91 ±0.10	93.77 ±1.73	17.66 ±1.24	0.048 ±0.01	13.27 ±0.27	16.32 ±0.30	21.61 ±0.43
Ar Rabwah	54.64 ±1.33	8.61 ±0.29	117.2 ±0.75	39.05 ±0.66	0.10 ±0.01	16.35 ±0.21	21.8 ±0.68	24.47 ±1.09
Al Malaz	13.17 ±0.30	9.52 ±0.30	170.5 ±1.06	38.02 ±0.96	0.072 ±0.01	23.32 ±0.39	32.32 ±1.29	34.98 ±1.39
Ar Rawdah	9.09 ±0.31	13.22 ±0.45	107.2 ±1.51	16.28 ±1.48	0.067 ±0.01	13.51 ±0.18	19.19± 0.60	25.11 ±1.09
An Namuthajiyah	58.24 ±0.39	14.77 ±0.55	231.8 ±4.00	90.17 ±2.10	0.125 ±0.02	33.15 ±0.66	42.54 ±1.90	47.02 ±2.19
An Nuzhah	11.53 ±0.17	6.68 ±0.17	96.49 ±0.46	13.02 ±0.65	0.05 ±0.01	14.66 ±0.55	19.23 ±0.53	16.14 ±0.64
Al `Aqiq	10.81 ±0.08	6.12 ±0.22	98.7 ±1.33	6.54 ±0.13	0.045 ±0.01	13.80 ±0.50	19.56 ±0.71	17.56 ±0.58

*Each concentration value is an average of five replicate measurements.

Cont., Table 3. Heavy metals concentrations in collected soil samples*.

District	Concentration (mg/kg dry soil)*						
	Co	As	U	Mo	Ag	Sn	Sb
Al Aziziyah	8.5 ±0.69	2.91 ±0.02	1.10 ± 0.05	0.84 ±0.01	0.51 ±0.02	1.55 ±0.05	0.26 ±0.01
Al Iskan 2	6.09 ±0.17	2.87 ±0.09	1.00 ±0.02	0.35 ±0.00	0.52 ±0.02	0.59 ±0.01	0.25 ±0.01
Al Iskan 1	7.6 ±0.37	2.88 ±0.09	1.16 ±0.03	0.55 ±0.02	0.55 ±0.00	0.94 ±0.06	0.30 ±0.01
Al Manakh	7.56 ±0.24	2.48 ±0.06	1.00 ±0.03	2.21 ±0.03	0.45 ±0.01	1.15 ±0.01	0.44 ±0.02
Ghubaira	7.39 ±0.27	2.66 ±0.06	0.90 ±0.03	0.52 ±0.01	0.43 ±0.02	1.02 ±0.03	0.48 ±0.01
Manfuhah	11.98 ±0.56	3.83 ±0.07	1.52 ±0.06	0.85 ±0.01	0.66 ±0.04	1.96 ±0.02	1.24 ±0.02
Al Mansurah	8.97 ±0.40	2.75 ±0.07	1.03 ±0.01	0.50 ±0.01	0.44 ±0.02	0.73 ±0.02	0.36 ±0.01
Al Khalidiyah	7.34 ±0.29	2.40 ±0.03	0.98 ±0.04	0.79 ±0.01	0.50 ±0.03	1.57 ±0.10	0.50 ±0.01
Ad Dar Al Baida	6.1 ±0.66	2.01 ±0.02	0.87 ±0.03	0.32 ±0.01	0.50 ±0.02	0.45 ±0.01	0.16 ±0.01
Al Ghanamiah	6.44 ±0.72	1.91 ±0.04	0.78 ±0.01	0.30 ±0.01	0.32 ±0.01	0.42 ±0.01	0.15 ±0.01
Old Manfuhah	7.19 ±0.10	2.16 ±0.09	0.91 ±0.03	1.13 ±0.15	0.51 ±0.02	1.22 ±0.05	0.80 ±0.04
Al Yamamah	10.11 ±0.46	3.85 ±0.04	1.54 ±0.03	0.70 ±0.01	0.68 ±0.02	0.87 ±0.01	0.44 ±0.01
Sultanah	10.07 ±0.88	3.67 ±0.06	1.33 ±0.03	0.69 ±0.01	0.57 ±0.02	0.70 ±0.02	0.31 ±0.01
Al Shifa	11.65 ±0.70	4.06 ±0.05	1.39 ±0.03	0.72 ±0.01	0.58 ±0.03	1.02 ±0.02	0.65 ±0.01
Al Masani`	8.25 ±0.78	2.56 ±0.03	1.15 ±0.01	0.47 ±0.02	0.56 ±0.01	1.47 ±0.04	0.32 ±0.01
Utaiqah	7.49 ±0.78	2.24 ±0.04	0.89 ±0.05	0.41 ±0.01	0.36 ±0.01	0.58 ±0.01	0.28 ±0.01
Al Shimaisi	11.46 ±0.83	3.4 ±0.05	1.26 ±0.06	1.09 ±0.02	0.64 ±0.01	1.32 ±0.03	0.67 ±0.01
Al `Ulayya	7.13 ±0.05	2.66 ±0.07	1.06 ±0.03	0.38 ±0.01	0.60 ±0.01	0.60 ±0.01	0.42 ±0.02
Al `Ulayya	6.44 ±0.21	2.35 ±0.05	1.00 ±0.04	0.53 ±0.01	0.71 ±0.01	0.64 ±0.01	0.49 ±0.01
Al Sulaymaniyah	8.1 ±0.26	2.82 ±0.06	1.00 ±0.01	0.41 ±0.01	0.61 ±0.02	0.57 ±0.02	0.41 ±0.01
Al Murabba`	9.13 ±0.25	3.22 ±0.05	0.96 ±0.01	1.17 ±0.22	0.52 ±0.01	1.18 ±0.07	0.60 ±0.05
Al Wurud	10.56 ±0.31	3.8 ±0.05	1.16 ±0.05	0.77 ±0.02	0.54 ±0.03	1.95 ±0.03	1.22 ±0.02
Al Jazirah	4.81 ±0.35	2.05 ±0.04	0.66 ±0.01	0.38 ±0.02	0.35 ±0.02	0.45 ±0.02	0.25 ±0.02
Ar Rabwah	6.3 ±0.22	2.85 ±0.09	0.83 ±0.04	0.47 ±0.01	0.40 ±0.02	0.70 ±0.02	0.49 ±0.01
Al Malaz	8.73 ±0.27	3.42 ±0.02	1.26 ±0.04	0.59 ±0.03	0.44 ±0.02	0.72 ±0.04	0.44 ±0.01
Ar Rawdah	5.71 ±0.18	2.43 ±0.05	0.82 ±0.01	0.34 ±0.01	0.50 ±0.01	0.56 ±0.02	0.19 ±0.01
An Namuthajiyah	10.92 ±0.39	4.44 ±0.14	1.22 ±0.02	0.62 ±0.01	0.42 ±0.02	0.95 ±0.03	0.44 ±0.02
An Nuzhah	5.1 ±0.14	1.61 ±0.02	0.58 ±0.01	0.28 ±0.01	0.36 ±0.02	0.52 ±0.01	0.24 ±0.01
Al `Aqiq	5.56 ±0.15	1.86 ±0.03	0.88 ±0.03	0.29 ±0.01	0.35 ±0.01	0.41 ±0.02	0.18± 0.01

*Each concentration value is an average of five replicate measurements.

Table 4. Heavy metals concentrations likely to exist in soil as (mg/kg) dry soil (Sezgin *et al.*, 2003).

Element	Concentrations (mg/kg)	Acceptable values (mg/kg)	Maximum Values (mg/kg)
Pb	0.1-20	100	100
Cd	0.1-1	3	3
Cr	10-50	100	100
Cu	5-20	50	100
Ni	10-50	50	50
Zn	10-50	300	300
Co	1-10	50	-
Mo	1-5	5	-
As	2-20	20	-
V	10-100	50	-
U	-	5	-

Yamama Cement Company and industrial area on Al Kharj Road. Furthermore there are small and medium industrial facilities (e.g. automotive repair workshops), so it can be concluded that most of the zinc contamination was a results of airborne deposition from industrial sources. Moreover, car tires contain significant quantities of zinc, which may contaminate soils near roads.

Copper (Cu): Cu concentrations ranged between 9.92 and 19.78 mg/kg in dry soil samples, with an average concentration of 9.92 mg/kg dry soil. The highest concentration (19.78 mg/kg dry soil) is almost equal to the Cu maximum concentration (20 mg/kg dry soil) found in typical soils, and well below the acceptable limit (50 mg/kg dry soil) and the allowable limits (100 mg/kg dry soil) (Sezgin *et al.*, 2003). The highest Cu concentrations were found at schools playgrounds in Al Manakh (19.78 mg/kg dry soil), Al Wurud (19.56 mg/kg dry soil), and Manfuhah (16.37 mg/kg dry soil). Al Manakh's playground is located on Al Kharj Road and in an industrial area with very heavy traffic density, and is about 1 km away from the Yamama Cement Company and about 0.5 km away from the National Gypsum Company. This might indicate that the elevated concentrations of Cu are resulting from airborne deposition from surrounding industrial sources. Expected Cu sources are automobile radiator, engine components, thrust bearings and bearing metals (Sezgin *et al.*, 2003).

Cadmium (Cd): measured Cd concentrations were in the range of 0.05 to 0.35 mg/kg in dry soil samples, with an average concentration of 0.12 mg/kg dry soil. The highest Cd concentration (0.35 mg/kg dry soil) within the typical range (0.1-3 mg/kg dry soil) found in soils and is well below both the acceptable limits and maximum concentration of 3 mg/kg dry soil (Sezgin *et al.*, 2003). The highest cadmium concentrations in soil samples have been found at schools playground in Al Wurud (0.35 mg/kg dry soil), Manfuhah (0.24 mg/kg dry soil), Al Shifa (0.19 mg/kg dry soil), Al Shimaisi (0.19 mg/kg dry soil), Ghubaira (0.17 mg/kg dry soil), and Al Murabba (0.17 mg/kg dry soil).

Nickel (Ni): Nickel concentrations were in the range of 10.03 to 33.15 mg/kg in dry soil samples, with an average concentration of 17.45 mg/kg dry soil. The highest Ni concentration (33.15 mg/kg dry soil) is within the typical range of this heavy metal found in soils (10-50 mg/kg dry soil), and is below the acceptable and maximum concentration of 50 mg/kg dry soil (Sezgin *et al.*, 2003). The highest Ni concentrations in soil samples have been found at schools playground in An Namuthajiyah (33.15 mg/kg dry soil), Al Shifa (26.91 mg/kg dry soil), Sultanah (24.51 mg/kg dry soil), Al Malaz (23.32 mg/kg dry soil), and Manfuhah (22.88 mg/kg dry soil).

Chromium (Cr): Cr concentrations ranged between 16.14 and 47.02 mg/kg in dry soil samples, with an average concentration of 29.36 mg/kg dry soil. The highest Cr concentration (47.02 mg/kg dry soil) is very close to the maximum concentration (50 mg/kg dry soil) found in typical soils, and is two times lower than the maximum allowable limit of 100 mg/kg dry soil (Sezgin *et al.*, 2003). The highest Cr concentrations in soil samples were measured at the schools playground of An Namuthajiyah (47.02 mg/kg dry soil), Al Shifa (43.54 mg/kg dry soil), Manfuhah (42.81 mg/kg dry soil), Al Yamamah (41.78 mg/kg dry soil), Al Shimaisi (39.6 mg/kg dry soil) and Al Wurud (38.08 mg/kg dry soil).

Cobalt (Co): measured Co concentrations ranged between 4.81 and 11.98 mg/kg in dry soil samples, with an average concentration of 8.02 mg/kg dry soil. The highest Co concentration (11.98 mg/kg

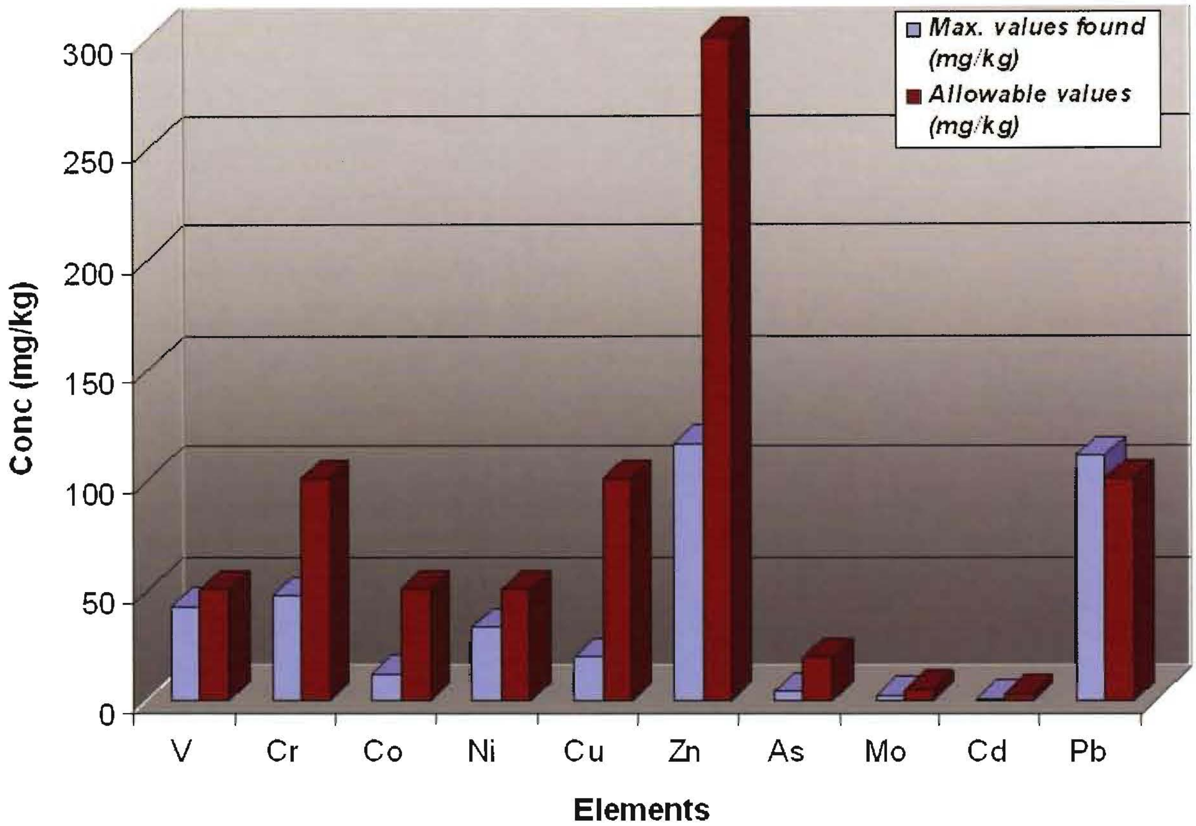

Fig. 4. Comparison between the maximum concentrations found in the soil samples and the maximum allowable limits according to Sezgin *et al.*, 2003.

dry soil) is slightly higher than the maximum Co concentration found in soils (10 mg/kg dry soil), but well below the acceptable and maximum values of Co of 50 mg/kg dry soil (Sezgin *et al.*, 2003). The highest Co concentrations in soil samples were found at schools playground in Manfuhah (11.98 mg/kg dry soil), Al Shifa (11.65 mg/kg dry soil), Al Shimaisi (11.46 mg/kg dry soil), An Namuthajiyah (10.92 mg/kg dry soil) and Al Wurud (10.56 mg/kg dry soil).

Arsenic (As): measured As concentrations were in the range of 1.61 to 4.44 mg/kg in dry soil samples, with an average concentration of 2.83 mg/kg in dry soil. The highest As concentration (4.44 mg/kg dry soil) is within the range found in typical soils (2-20 mg/kg dry soil), and is well below the acceptable limit of 20 mg/kg dry soil (Sezgin *et al.*, 2003). The highest As concentrations in soil samples were measured at schools playground in An Namuthajiyah (4.44 mg/kg dry soil), Al Shifa (4.06 mg/kg dry soil), Al Yamamah (3.85 mg/kg dry soil), Manfuhah (3.83 mg/kg dry soil) and Al Wurud (3.80 mg/kg dry soil). Figure 4 illustrates a comparison between the maximum concentration levels detected in this study with the maximum allowable limits of some heavy elements concentrations in the soil obtained from literature (Sezgin *et al.*, 2003). The figure indicates that the concentration levels for most of the heavy metals are below the allowable concentration limits, except for Pb. A convenient way to assess trace metal buildup in a particular region is to calculate the ratios of the concentration values of concerned elements (M_{obs}) to their average concentration in the earth's crust (M_{crust}) A value of unity or less for this ratio for a given element should, in principle, indicate no or insignificant natural or anthropogenic enrichment of that element in the studied region with respect to global average (Wei and Haraguchi, 1999). The calculated enrichment coefficient values (M_{obs}/ M_{crust}) for V, Cr, Mn, Co, Ni, and Cu were less than unity at 0.32, 0.47, 0.25, 0.51, 0.44 and 0.36, respectively, which suggests that the origin of these elements is mostly the local soil. On the other hand, the enrichment coefficient values for Zn and Pb were more than unity at 1.66 and 8.47, respectively, suggesting that these elements are anthropogenic in origin, e.g., from the traffic emission.

Conclusion

Based on the results obtaind from the measurements of the concentrations of the heavy metals at twenty nine schools playground in selected districts in Riyadh City, it can be generally concluded that schools playgrounds with elevated heavy metals contents are found to be located near main roads leading to high traffic emissions. In addition, some of these affected schools playgrounds are located close to industrial areas and other are in the middle of high residential sites. Furthermore, the soil texture of the playground plays an important role in the ability of the soil in absorbing the heavy metals, and therefore, it acts as a storage reservoir for both water and pollutants, especially in the case of sandy clay loam soil. It can also be concluded that the concentration levels for all elements in all soil samples were below the allowable concentration limits except for Pb. The measured Pb concentration exceeded the allowable concentration limits, in Manfuhah school playground, despite using unleaded gasoline in Saudi Arabia since January 2001. This may be due to previous accumulations of the element prior to the use of unleaded gasoline.

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