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Assessment of Roadside Soil Pollution by Heavy Metal Ions and Correlation to Traffic Activities in Madina City, Saudi Arabia: Part I

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Traffic activities are considered as one major sources of heavy metal pollution in roadside soil. Therefore, this study was carried out to investigate the impact of traffic on the characteristics of heavy metals in roadside soil of Madina city, Saudi Arabia. Soil samples from the surface and 20 cm under surface in 12 different sites were collected and analyzed for As, Co, Pb, V and Zn. The traffic density was monitored in roads near the sampling sites and correlated with heavy metal concentration to investigate the impact of traffic density on heavy metal ions concentration. The results revealed great dependence of Pb and Zn on traffic density with correlation coefficients of 0.991 and 0.987, respectively. The other metals, As, Co and V showed no dependence on traffic density and no dependence between the surface and under surface concentration. The values of pollution indices such as contamination factor, degree of contamination and geo-accumulation index (I_{geo}) indicated various levels of contamination in the roadside soil in some study sites. The degree of contamination values in the more polluted site were 32.192, 28.872 and 23.902 in the airport road (1), Taibah University street (2) and Orwah valley street (3). These results ensure that traffic emissions, automobiles and other anthropogenic activities are major sources of the metal contamination.

Keywords: Heavy metal ions, Soil pollution, Traffic impact on pollution, Al-Madinah.

INTRODUCTION

Nowadays, the world is facing an unprecedented environmental crisis where the deterioration of the Earth's environment increasingly threatens the natural resources. The pollution caused by heavy metal ions is considered as one of the most serious environmental problems[1]. Heavy metal ions are characterized by their mobility in the eco-system and by their toxicity to higher life forms even at low concentration[2]. In addition, these ions are indestructible, thus persistent in the environment and undergo a bioaccumulation processes along the food chain, leading to both ecological and health problems[3,4]. Accordingly and due to their toxicity especially arsenic[2] and lead ions, persistence and non-degradability characteristics, it is of great importance to monitor the heavy metals concentrations in roadside environments[5].

In urban areas, the main anthropogenic sources of heavy metal pollution include: industries, traffic, mining activities, smelters, domestic heating, waste incineration, construction road infrastructure[6]. The traffic source includes vehicles parts such as tyre wear, brake linings, fuel combustion and others. On the other hand, the road infrastructure includes pavement wear, corrosion of galvanized steel, crash barriers, corrosion of batteries and metallic parts such as radiators and others[7,8]. Traffic-related elements such as platinum group elements (PGEs), zinc and copper have shown sharp decrease in concentration with increasing distance from the traffic lane[9]. Heavy metal ions are produced from the above activities and are sent into the air then the metal ions subsequently are deposited into nearby soils[10]. Consequently, there is a close relationship between metal ions concentration in roadside soil and those in the dust falls[11]. Moreover, these heavy metal ions can also affect the air quality by generating airborne particles and dusts[12]. For these reasons, street dusts and top roadside soils in urban areas are indicators for the pollution by heavy metal ions contamination from atmospheric deposition[13].

In the last two decades, most countries have started to reduce, regulate and set up upper limits for the heavy metal ions levels in the environment[14]. Thus, literature has seen an upsurge of research studies dealing with metal pollution in urban environment especially in roadside soil. However, most of these studies have been carried out in developed countries and only few studies have been conducted in developing countries[6,15-21]. Most of the efforts in these studies were made in assessing heavy metals concentration in the roadside soil[7], atmosphere[10] and plants[22]. Some studies investigated the relation between heavy metals concentration and distance from the road[5] and the traffic volume[9,23].

In Saudi Arabia, limited research has been carried out concerning chemical contamination in roadside soil[23]. Al-Shayeb and Seaward[24] determined the concentration of the metals Pb, Zn, Cu, Cr and Ni in roadside surface and sub-surface. They reported that level of Pb, Zn and Cu correlated well with traffic intensity. Zinc level was also measured since it represents a product of tyre tare on roads[25]. Madinah is the second holiest place for Muslims. This holy city receives more than 13 million visitors every year. As a result, human and traffic activities in the center of the city is significantly large. However, no monitoring of trace metal ions in roadside soil or atmosphere has been carried out yet. For this reason, this study was devoted to investigate heavy metal ion content in the roadside of Madinah, in which exists the second holiest mosque for Muslims. The results were correlated with traffic intensity in these roads. These results will help the local government to take some measures to control and organize the traffic movements in the city.

EXPERIMENTAL

Sampling area: Medina first is located in the western region of Saudi Arabia, 150 km east of the Red Sea and on the longitudes (39 42 36 – 39 96 00) and latitude (24 36 00 – 24 21 00). Medina's area is about 589 km^2 of which 293 km^2 is considered as urban area, while the rest is outside the urban area. The city height is 608 meters above the sea level. Madinah and its surrounding areas are composed of mountains, valleys, slopes of desert and other agricultural lands, in addition to the highway network. The population of Madinah is 1.7 million people, with a population density of about 1,868 inhabitants/km^2. Medina's soil is formed from silt and sand pebble in addition to the barren rocks. In the south of the city sand and ancient rocks have turned into silt due to erosion. This effect has made the southern area of the city more suitable for agriculture than the north. Most of the urban area in the heart of the city is located on the soil of heavy fabric.

All soil samples were collected from different roadsides of Madinah (Table-1). The sampling sites are distributed evenly in all directions of the city and were selected to cover most crowded streets in and around the city including those having heavy and light traffic. The names and a brief description of the sampling sites are given Table-1. During the sampling process, twelve soil samples (humus) were carefully collected from the surface of roadsides and another twelve samples were collected from points 20 cm under the ground surface.

Chemicals of analytical grade were used as received in this investigation. The tested heavy metal ions were As, Co, Ni, Pb and Zn. and a stock solutions (1000 µg mL^{-1}, BDH, Poole, England) of these ions were used to prepare diluted solutions. In the digestion process for the collected soil samples and the certified reference material (IAEA-soil-7), concentrated HF, HCl and HNO_3 (Merck, Darmstadt, Germany) were used. Low density polyethylene (LDPE) bottles were used to keep ions solutions. These bottles were carefully cleaned first with hot detergent, then soaked in 50 % w/v HCl, 0.2 M HNO_3 then washed by 0.5 M HCl and finally rinsed with deionized water. The glassware's used in all experiments were cleaned by immersing them in 1.5 % w/v HNO_3 for 24 h before use.

TABLE-1
DESCRIPTION OF THE SAMPLING SITES IN MADINA ROADS AND STREETS

Site No.	Sampling site	Description of the sampling area	Traffic Cars/day
1	West airport road	Sandy soil, heavy traffic	36768
2	West to Taibah University	Sandy soil and somewhat harsh, heavy traffic	33480
3	Orwah valley street	Clay soil	21744
4	Qubaa municipality	Muddy soil	16416
5	East Al-Haram area	Sandy soil, old buildings were removed	15144
6	Legend Hall street	Clay soil and easy drilling	12624
7	Oyon street	Near valleys, muddy soil, easy to drill, high traffic	10032
8	West Al-Haram area	Used as parking lots for cars, medium sandy earth	6960
9	Walking street	Easy to soil, presence of rigs, traffic	5112
10	Al-Ansar area	Agricultural land, the soil sample was wet	4992
11	East airport road	Sandy soil	768
12	Land near Rashed Mall	Rocky ground	216

Soil sample analysis: Soil samples were prepared according to the method of Narin *et al.*[26]. The soil samples were heated for 2 h and dried at 110 °C, then grounded and sieved using a 200 mesh. A 0.50 g of the prepared soil sample was digested using the microwave digestion method. The microwave digestion system, Milestone ETHOS lab station with easy WAVE or easy CONTROL software HPR1000/10S high pressure segmented rotor, was used for soil samples digestion procedures by acids. This method of acid digestion of the soil sample in a closed vessel device with temperature control in a microwave is suitable for metal determination by spectroscopic methods. The TFM vessel was placed on on the balance plate and the 0.50 g of the sample was weighed, then the TFM vessel was introduced into the HTC safety shield. After the addition of 9 mL of 37 % HCl and 3 mL of 65 % HNO_3 the solution was gently swirled and homogenized. After that the vessel was closed and then introduced into the rotor segment, then tighten by using the torque wrench. The segment was inserted into the microwave cavity and the temperature sensor was connected. Finally, the microwave program was run to completion. After that the rotor was cooled by air until the solution reaches room temperature, then the vessel was opened and transferred to a marked flask. The system allows the digestion of four samples at the same time. Three different digestion programs labeled as P1, P2 and P3 were tested with the SRMs[27]. Combinations of 65% HNO_3 which was used for easily oxidizable material, 40 % HF which was used for extraction of inorganic matrixes and 37 % HCl were added to each of the digestion vessels.

The details of the heating programs used are as follows: step one continues 10 min. with temperate of 200 °C and Microwave power up to 1000 watt. On the other hand step two used the same conditions but continues for 15 min. The digestate obtained were then filtered through a 0.45 μm membrane filter, diluted to 10 mL and stored for further analyses. For accurate results, all the extraction procedures were applied in triplicate.

The accuracy and precision of analytical experimental results were checked using a standard reference material (IAEA Soil-7, International Atomic Energy Agency). The results obtained by proposed procedures of the digestion and analysis are shown in Table-2. It is clear from Table-2 that there is a good agreement among experimental and certified values. This confirms the suitability and applicability of the applied digestion procedure of soil samples.

TABLE-2
ANALYTICAL DATA OF SOME SELECTED METAL IONS IN THE CERTIFIED REFERENCE MATERIAL (IAEASOIL-7) BY THE EMPLOYED DIGESTION PROCEDURE AND THE ICP-MS*

Element	Certified values concentration (ppm)	95 (%) Confidence interval	Present work, ICP-MS concentration (ppm)
As	13.4	12.5-14.2	15.4 ± 0.0
Co	11.51	10.5-15.5	14.1 ± 0.005
Pb	12.1	10.2-14.3	12.6 ± 0.003
V	36.2	32.4-45.8	37.2 ± 0.004
Zn**	60.5	57.3-65.4	62.0 ± 0.04

*Average of five measurements ± relative standard deviation

Traffic density: Traffic density information was obtained by a team of workers who were distributed in the streets from where soil samples were obtained. In each point two workers were assigned to count the traffic in both sides of the road for a period of 1 h. The whole team started at the same time in all the 12 places and repeated the process three times to obtain a mean value. These values are tabulated in Table-1 and used in the correlation step.

Instrumental analysis: In this investigation, an ICP-mass spectrometry (ICP-MS) Perkin-Elmer Sciex (model Elan DRC II, USA) and a Perkin Elmer inductively coupled plasma-optical emission spectrometer (ICP-OES) model optima 4100 DV, USA, spectrometers were used to measure the heavy metals concentration in the test samples. The ICP-MS analyzer was optimized every day before use and operated as recommended by the manufacturers catalogues. A Milli-Q Plus system (Millipore, Bedford, MA, USA) was operated to obtain deionized water used in the preparation of the standard solutions for all ions.

Soil contamination level with heavy metal ions: Roadside soil contamination with heavy metal ions is an important parameter in the assessment process of the pollution of urban areas by traffic and human activities. In this investigation, the contamination level was calculated using indices proposed by Hakanson[28]. These indices are the contamination factor (CF) and integrated degree of contamination, CD. These indices are defined as follows:

$$CF = C_m/C_b \quad (1)$$

$$CD = \Sigma CF \quad (2)$$

where, C_m is the measured heavy metal concentration, μg/g and C_b is the reference concentration of the heavy metals in the uncontaminated soil, μg/g. According to Molawa *et al.*[29] the contamination levels were classified into four categories as follows: low, moderate, considerable and very high for $CF < 1$, $1 \leq CF < 3$, ($3 \leq CF < 6$ and $6 = CF$, respectively. On the other hand, degree of contamination values will be divided into four categories to describe metal contamination levels in the sampling sites. These categories are as follows: low ($CD < 5$), moderate ($5 \leq CD < 10$), considerable ($10 \leq CD < 20$) and very high ($20 \leq CD$) degree of contamination[14]. If the degree of contamination values exceeded 20, then it was necessary to take immediate counter measures to reduce heavy metal contamination in the road dust.

In addition, the geo-accumulation (I_{geo}) index was defined by Müller[30] was used in this study. This index can be calculated using the following equation:

$$I_{geo} = \log 2[C_s/(1.5\ C_b)] \quad (3)$$

The factor 1.5 is introduced to eliminate the possible variations effects of reference values of a given metal in addition to minor anthropogenic influences. I_{geo} for each metal is classified into 5 grade-categories as follows: $I_{geo} < 0 \leq$ practically unpolluted; $0 < I_{geo} \leq 1$ = unpolluted to moderately polluted; $1 < I_{geo} \leq 2$ = moderately polluted; $2 < I_{geo} \leq 3$ = moderately to strongly polluted; $3 < I_{geo} \leq 4$ = strongly polluted; $4 < I_{geo} \leq 5$ = strongly to extremely polluted and $I_{geo} \geq 5$ = extremely polluted.

Statistical analysis: In this investigation, statistical analyses were performed using statistical package for Social Sciences (SPSS) program. The values of descriptive statistics parameters like mean, range and standard deviation were obtained. The correlation coefficients (r) between the heavy metal concentration and the traffic intensity were calculated by $p < 0.05$. In addition, the contamination ratio for each sampling site was calculated. The contamination ratio is defined as the ratio of the average metal concentration of a site to that of the metal of the reference site (control).

RESULTS AND DISCUSSION

Heavy metal concentration in roadside of Madinah soil: Most of the sites chosen for metal ion concentration measurement are considered as urban zone since these areas are characterized by high population density of more than 50 or more persons per hectare[31] in addition to high traffic density. Only site one is considered as a suburban zone because the population density is lower than this value.

As mentioned above, As, Co, Pb, V and Zn metals concentration were measured in 12 different sites of Madinah city. Table-3 shows some basic statistical parameters for the distribution of two arbitrary metals concentration in these sites. It is evident from Table-3 that the values of standard deviation as a measure of random error, are relatively low. These metals are cobalt and vanadium and the average values of triplicate measurements of these metals concentrations over soil surface and under soil surface were estimated in μg/g. In addition, all metal concentration measurements in addition to traffic intensity are presented in Figs. 1-5.

Fig. 1 shows the variation of arsenic ion concentration in samples taken from the surface and 20 cm under the surface in the 12 sites. In addition it shows the variation of traffic intensity in roads and streets near those sites. It should be noted that the sites are numbered according to the traffic intensity.

TABLE-3
SOME STATISTICAL ANALYSIS DATA FOR COBALT AND VANADIUM SAMPLES COLLECTED FROM SURFACE AND UNDER SURFACE IN 12 DIFFERENT SITES OF MADINA CITY

Site	Place	Cobalt			Vanadium		
		Mean (µg/g)	S.D.	%RSD	Mean (µg/g)	S.D.	%RSD
1	OS	15.2	0.0028	0.93	85.85	0.0232	1.35
	US	13.9	0.0017	0.63	67.4	0.0217	1.57
2	OS	8.5	0.0017	1.02	37.2	0.0053	0.71
	US	12.25	0.0007	0.3	57.45	0.0129	1.12
3	OS	10.35	0.002	0.96	59.3	0.0166	1.4
	US	12.85	0.0025	0.96	83.1	0.0166	1
4	OS	11.45	0.002	0.88	55.4	0.0038	0.34
	US	12.5	0.0019	0.76	68.4	0.0078	0.57
5	OS	7.3	0.0014	0.98	27.85	0.0107	1.92
	US	8.75	0.0022	1.24	42.9	0.0099	1.16
6	OS	15.05	0.002	0.67	71.2	0.0192	1.35
	US	12.85	0.0024	0.92	65.75	0.0114	1.09
7	OS	12.8	0.0011	0.43	66.95	0.0074	0.56
	US	11.7	0.0018	0.76	66.1	0.0158	1.2
8	OS	10.6	0.0021	1.01	55.6	0.0034	0.3
	US	11.65	0.002	0.85	70.65	0.004	0.28
9	OS	16.8	0.0022	0.66	78.2	0.0077	0.5
	US	15.3	0.0007	0.23	69.2	0.0036	0.26
10	OS	11.4	0.0019	0.85	151.4	0.0004	0.01
	US	7.05	0.0006	0.44	44.55	0.01	1.12
11	OS	10.6	0.0016	0.77	53.15	0.0019	0.18
	US	12.3	0.0052	2.12	63.95	0.0059	0.46
12	OS	17.3	0.0029	0.84	74.4	0.0299	2.01
	US	17.8	0.0058	1.64	153.45	0.0555	1.81

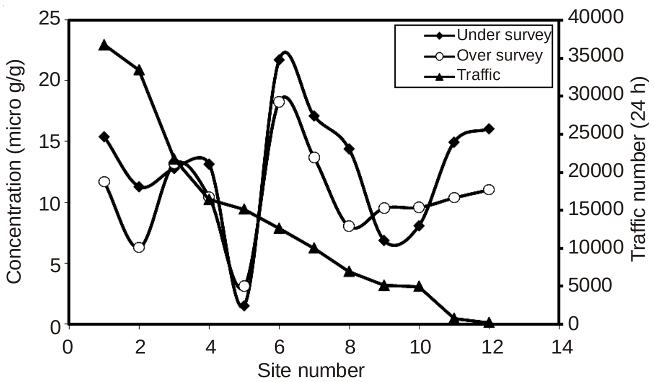

Fig. 1. Variation of arsenic, surface and under surface concentration and traffic density across the sampling site

Site number 1 has the highest traffic intensity and site 12 has the lowest traffic intensity. It is evident from Fig. 1 that As concentration in these sites ranges from 3.1 to 18.3 and from 1.55 to 17.1 µg/g in surface and under surface samples, respectively. It is familiar that arsenic is widely distributed in the earth's crust in the form of minerals, such as realgar (As_4S_4), orpiment (As_2S_3), arsenolite (As_2O_3) and in its elemental form to a small extent[31]. Its average concentration is about 3.4 µg/g[32]. As noted from Fig. 1 the values of arsenic concentration in some sites of Madinah soil are higher than those cited[31]. However, there is no indication that traffic has any influence on arsenic concentration. As Fig. 1 shows that heavy traffic sites have relatively the same concentration of arsenic as low traffic sites have. Arsenic is usually released to the environment from both natural and anthropogenic sources. Natural sources include wind-blown soil and volcanoes. On the other hand, anthropogenic sources metal mining and smelting, pesticide application, coal and wood combustion and solid waste incineration[32].

Fig. 2 shows the variation of cobalt metal concentration in samples taken from the surface and 20 cm under the surface in the 12 sites. It is evident from Fig. 2 that in these sites. Cobalt concentration ranges from 7.3 to 17.3 and from 7.05 to 17.8 µg/g in surface and under surface samples, respectively. These values are within the normal range of cobalt concentration in the earth's crust which is about 20-25 µg/g[33]. In addition, the values of cobalt in surface and under surface samples are comparable in all the 12 sites, which means that there is no effect of the traffic intensity level on Madina soil.

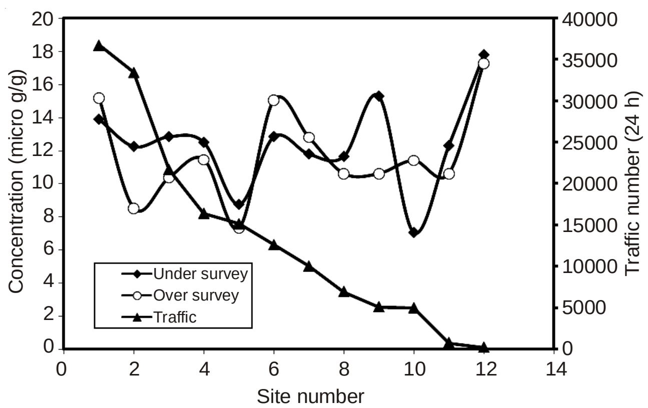

Fig. 2. Variation of cobalt, surface and under surface concentration and traffic density across the sampling site

Fig. 3 shows the variation of Pb metal concentration in samples taken from the surface and 20 cm under the surface in the 12 sites. It is evident from Fig. 3 that in these sites, lead concentration ranges from 1.3 to 33.35 and from 0.1 to 3.3 µg/g in surface and under surface samples, respectively. It is evident from Fig. 3 that Pb concentration levels in all sites clearly reflect the impact of traffic intensity in these sites. For example sample 1 represents soil samples obtained from the airport road has the highest Pb concentration of 33.35 µg/g and the highest traffic intensity of 36768 vehicle/24 h. In addition, Pb concentration in under surface samples is low compared to the surface samples, but it reflects again the impact of traffic intensity. These results are in agreement with those of Al-Shayeb and Seaword[24] and Kadi[34] who studied the impact of traffic on heavy metal concentration in roadside soil in Jeddah city and Riyadh city, Saudi Arabia and with many other investigations in many cities around the world. However, The values of Pb concentration in Madinah city is low compared to those of Riyadh and Jeddah cities. The maximum Pb concentration in Madinah, Riyadh and Jeddah were 33.35, 123.28 and 104.86 µg/g, respectively. This fact could be attributed to two reasons: Studies of Al-Shayeb and Seaward[24] and Kadi[34] were conducted since 11 and 5 years, respectively. At those days leaded gasoline was not phased out yet. In addition, Riyadh and Jeddah cities are more crowded than Madinah city with more traffic density.

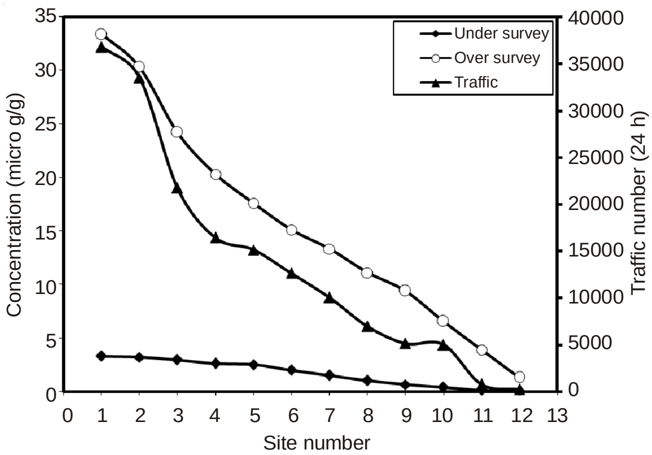

Fig. 3. Variation of lead, surface and under surface concentration and traffic density across the sampling site

It should be noted that lead is a naturally occurring highly toxic metal found in the Earth's crust in small amounts at about 15-20 µg/g in some places. Moreover, lead rarely occurs in its elemental state, but it rather occurs in its +2 oxidation state in many compounds such as galena (PbS), anglesite ($PbSO_4$) and cerussite ($PbCO_3$). Lead in soil comes from many household and industrial products like paint, solder, batteries and brass. In addition, it comes from the deposits left by automobile exhaust when leaded gasoline was widely used[35].

Fig. 4 shows the variation of vanadium metal concentration in samples taken from the surface and 20 cm under the surface in the 12 sites. It is evident from Fig. 4 that in these sites, vanadium concentration ranges from 27.58 to 85.85 and from 44.55 to 83.1 µg/g in surface and under surface samples, respectively. These values are within the normal range of vanadium concentration in the earth's crust which ranges from 3-310 µg/g and could reach 400 µg/g in areas polluted by fly

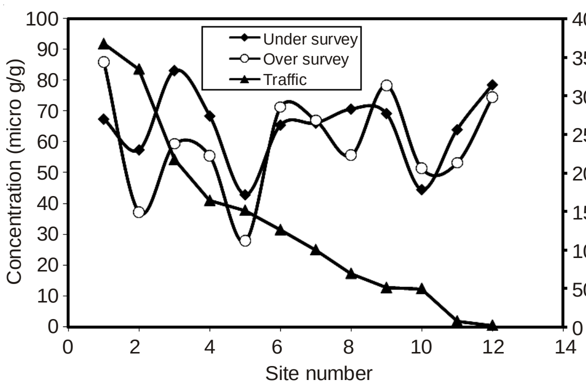

Fig. 4. Variation of vanadium, surface and under surface concentration and traffic density across the sampling site

ash[36,37]. Moreover, the values of vanadium in surface and under surface samples are comparable in all the 12 sites. This indicates no dependence on traffic intensity its level in madina soil.

Fig. 5 shows the variation of zinc metal concentration in samples taken from the surface and 20 cm under the surface in the 12 sites. It is evident from Fig. 5 that in these sites, zinc concentration ranges from 16.5 to 90.5 and from 10.5 to 49.75 µg/g in surface and under surface samples, respectively. Moreover, Fig. 5 shows that Zn concentration levels clearly reflect the impact of traffic intensity in these sites. For example sample 1 which represents soil samples obtained from the airport road has the highest Zn concentration of 90.5 µg/g where the highest traffic intensity of 36768 vehicle/24 h. In addition, Zn concentration in under surface samples is low compared to the surface samples, but it reflects again the impact of traffic intensity. These results are in agreement with those of Al-Shayeb Seaward[24] and Kadi[34] for zinc concentration in roadside soil in Jeddah city and Riyadh city, Saudi Arabia and with many other investigations in many cities around the world. However, The values of Zn concentration in Madinah city is relatively low compared to those of Jeddah city. The maximum Zn concentration in Madinah, Riyadh and Jeddah were 90.5 and 146.42 µg/g. This fact could be attributed to the that Jeddah city is more crowded than Madinah city and has higher traffic density.

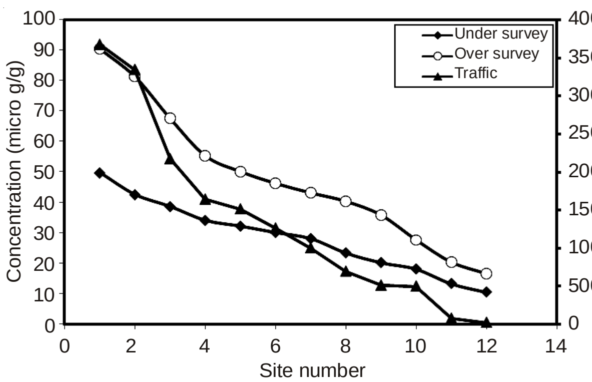

Fig. 5. Variation of zinc, surface and under surface concentration and traffic density across the sampling site

Zinc concentration in soil is usually low and it does not pose a toxicity problem in the environment[38]. Toxic quantities of zinc in soil are mainly attributed to anthropogenic sources[39]. As mentioned above, the highest value of zinc concentration in this study was 90.5 and the lowest value was 10.5 µg/g. These values are quite high as compared to national environmental quality standard range *i.e.* 5 µg/g[40].

Correlation between metals concentration and traffic density in Madinah city: Inter-correlation calculations using pearson correlation coefficient, r, between the surface heavy metals concentration of the 12 sites and traffic density are shown in Table-4. It is familiar that this coefficient measures the strength of a linear relationship between any two variables. Its scale ranges from -1 for a perfect inverse relationship, through 0 when there is no relationship to +1 for a perfect sympathetic relationship. In this study, the raw geochemical data were used in calculating the correlation coefficient using the SPSS (Statistical Program for the Social Sciences) computer software package (SPSS Inc., version 16.0). The results in Table-4 showed significant positive correlations ($p < 0.05$) are present between traffic density (TD), with both Pb and Zn. The correlation values are TD/Pb ($r = 0.991$) and TD/Zn ($r = 0.987$). This significant positive correlations between Pb and Zn metals with traffic density indicate possible contamination of the roadside soil by traffic emissions. In addition, Table-4 indicates some elemental pairs for example, Pb/Zn ($r = 0.996$), Co/As ($r = 0.69$), have strong correlation with each other. On the other hand, pairs such as Co/V ($r = 0.398$) and V/As ($r = 0.305$ have moderate interdependence. Moreover, pairs of Pb/As, Pb/Co, TD/As and TD/Co show no significant correlation with each other. The results concerning Pb and Zn with traffic density are in agreement with those of Al-Shayeb and Seaward[24], Kadi[34] and many other investigations. It could be concluded that road side soil contamination by the heavy metals originated from a common anthropogenic sources in addition to local industries since Madina city area has no heavy or major industrial development.

Inter-correlation calculations was made between metal concentration on the surface and under surface. The correlation values were: As(OS)/As(Us) ($r = 0.852$), Co(OS)/As(Us) ($r = 0.592$), Pb(OS)/As(Us) ($r = 0.963$), V(OS)/As(Us) ($r = -0.02$) and Zn(OS)/As(Us) ($r = 0.987$). These results indicate that each metal has strong correlation between its over and under surface concentration except vanadium metal.

Madina soil contamination level with heavy metal ions: It is clear from the above results that arsenic, lead and zinc concentration values in madina roadside soil are above the normal levels. Accordingly, the contamination level of these metals will be considered by calculating the contamination factor and integrated degree of contamination, degree of contamination in addition to the geo-accumulation, I_{geo}.

Table-5 shows the values of the contamination factor, the degree of contamination and the geo-accumulation, I_{geo} due to heavy metals. The contamination factor indicated very high contamination level ($6 \leq CF$) of Pb in sites from 1 through 9 and considerable contamination ($3 \leq CF < 6$) in sites 10 and 11 and finally moderate contamination ($1 \leq CF < 3$) in site number 12, the contamination factor of arsenic indicated moderate contamination ($1 \leq CF < 3$) in sites 1, 3, 6, 7 and 12 and low contamination ($CF < 1$) in sites 2, 4, 5, 8, 9, 10 and 11. On the other hand, the contamination factor of zinc indicated considerable contamination levels ($3 \leq CF < 6$) in sites 1 through 5, moderate contamination level ($1 \leq CF < 3$) in sites 6 through 11 and moderate contamination ($1 \leq CF < 3$) in site number 12.

The values of degree of contamination estimated for each site is shown in Table-5. It is clear from Table-5 that sites 1, 2 and 3 showed high degree of contamination (20 = CD), sites

TABLE-4
CORRELATION ANALYSIS AMONG METALS CONCENTRATION AND TRAFFIC DENSITY

Parameter	Traffic volume	As	Co	Pb	V	Zn
Traffic volume	1					
As	-0.077	1				
Co	-0.132	0.690	1			
Pb	0.991	-0.06	-0.213	1		
V	-0.242	0.305	0.398	-0.297	1	
Zn	0.987	-0.049	-0.172	0.996	-0.273	1

TABLE-5
CONTAMINATION FACTOR (CF), DEGREE OF CONTAMINATION (CD) AND GEO-ACCUMULATION INDEX (I_{geo}) OF POTENTIAL TOXIC METALS IN ROADSIDE DUSTS ALONG THE ROAD SECTION

Site number	As		Pb		Zn		CD
	CF	I_{geo}	CF	I_{geo}	CF	I_{geo}	
1	1.058	0.146	25.65	1.534	5.485	0.864	32.193
2	0.635	-0.072	23.31	1.492	4.927	0.818	28.872
3	1.19	0.200	18.615	1.395	4.097	0.737	23.902
4	0.946	0.100	15.615	1.318	3.352	0.65	19.913
5	0.28	-0.428	13.538	1.256	3.036	0.607	16.854
6	1.656	0.344	11.615	1.19	2.8	0.572	16.071
7	1.24	0.218	10.231	1.135	2.612	0.542	14.083
8	0.728	-0.013	8.538	1.056	2.442	0.513	11.708
9	0.864	0.061	7.231	0.984	2.17	0.461	10.265
10	0.869	0.064	5.038	0.827	1.672	0.348	7.579
11	0.941	0.098	3.000	0.602	1.23	0.215	5.171
12	1.000	0.124	1.000	0.124	1.000	0.124	3.000

from 4 through 9 showed considerable degree of contamination ($10 \leq CD < 20$), sites 10 and 11 showed moderate contamination and finally, site 12 showed low contamination. This indicates that long term exposure within the neighborhood of sites 1, 2 and 3 can lead to adverse health effects to human particularly on children, pregnant women and the aged who are all known to be vulnerable.

Table-5 shows the geo-accumulation index, Igeo which was calculated for three heavy metals, As, Pb and Zn. For As the pollution level obtained from this analysis indicates that three sites: 2, 5 and 8 are practically unpolluted ($I_{geo} < 0$) the other nine sites are unpolluted to moderately polluted ($0 < I_{geo} \leq 1$). In the case of lead, sites number 1 through 8 are moderately polluted ($1 < I_{geo} \leq 2$) and sites 9 to 12 are unpolluted to moderately polluted ($0 < I_{geo} = 1$). For zinc all sites are unpolluted to moderately polluted ($0 < I_{geo} = 1$). According to these results, the environment in the chosen sites is relatively more affected by Pb compared to Zn and As.

Conclusion

The result of the present study revealed the presence of the five heavy metals in Madina roadside soil in different levels. The concentrations were in the order of Zn > V > Pb > As > Co.

The present study was focused on the concentrations of Pb, Zn and their pollution levels in connection with traffic density. The concentration of these two metals showed a clear relationship with traffic conditions with correlation coefficients were 0.991 and 0.987, respectively. The most polluted roadside sites with lead and zinc were the airport road (1) and Taibah University road (2). The maximum contamination factor (CF) values for Pb, Zn were 25.65 and 5.485, respectively. This indicates very high contamination level with Pb and considerable contamination level with Zn in site 1. The maximum value of the degree of contamination (CD) was 32.192 in site 1 and showed high degree of contamination ($20 \leq CD$). This value showed considerable to the highest degree of contamination level. On the other hand the values of the index of geo accumulation (I_{geo}) for Pb and Zn in site 1 were 1.538 and 0.864, respectively. These values revealed that site 1 is moderately polluted ($1 < I_{geo} \leq 2$) with Pb and unpolluted to moderately polluted ($0 < I_{geo} \leq 1$) with Zn. The estimated results using the three indices are in good agreement in explaining the levels Pb and Zn metals present in the roadside soil samples and the good correlation with the traffic intensity. In further studies the effect of street crowdness and the presence of traffic signals on Pb and Zn in addition to other metal levels will be investigated. In addition more studies are required to investigate the real sources of pollutants in Madinah city.

REFERENCES

1. L.C. Mello, A. Claudino, I. Rizzatti, R.L. Bortoluzzi and D.R. Zanette, *J. Braz. Chem. Soc*., **16(3a)**, 308 (2005).
2. Z. Al-Qodah, *Desalination*, **196**, 164 (2006).
3. L. de Oliveria Franco, R. de Cussia C. Maia, A.L.F. Porto, A.S. Messias, K. Fukushima and G.M. de Campos-Takaki, *J. Microbiol*., **35**, 243 (2004).
4. T.R. Crompton, Toxicants in the Aqueous Echosystem, Wiley, Chichester, pp. 91-135 (1997).
5. X. Yan, D. Gao, F. Zhang, C. Zeng, W. Xiang and M. Zhang, *J. Environ. Res. Public Health*, **10**, 762 (2013).
6. S.P. Raj, *Res. J. Chem. Sci*., **3**, 18, (2013).
7. C. Pagotto, N. Remy, M. Legret and P. Le Cloirec, *J. Environ. Technol*., **22**, 307 (2001).
8. L.M.J. Dolan, H. Van Bohemen, P. Whelan, K.F. Akbar and V. O'mally, in eds.: J. Davenport and J.L. Davenport, Towards the Sustainable Development of Modern Road Ecosystem. In: The Ecology of Transportation: Managing Mobility for the Environment, Springer, Netherlands, pp. 275-331 (2006).
9. E.S. Abechl, O.J. Okunola, S.M.J. Zubairu, A.A. Usman and E. Apene, *Nigeria J. Environ. Chem. Ecotoxicol*., **2**, 98 (2010).
10. K.I. Sakagami, R.Eamada and T. Kurobe, *J. Mitteeilungen der DeutschenBodenkundlichenGesellscaft*., **33**, 59 (1982).
11. C.W. Gray, R.G. Mclaren and A.H.C. Roberts, *J. Sci. Total Environ*., **305**, 105 (2003).
12. X. Li, C. -Poon and P.S. Liu, *J. Geochem*, **16**, 1361 (2001).
13. L. Poggio, B. Vrscaj, R. Schulin, E. Hepperle and F.A. Marsan, *J. Environ. Poll*., **157**, 680 (2009).
14. M. Soylak, I. Narin, L. Elci and M. Dogan, *Fresenius Environ. Bul*., **9**, 36 (2000).
15. I. Narin, M. Soylak and M. Dogan, *Fresenius Environ. Bull*., **6**, 749 (1997).
16. G. Shi, Z. Chen, S. Xu, J. Zhang, L. Wang, C. Bi and J. Teng, *Environ. Pollut*., **156**, 251 (2008).
17. K.F. Akrari, W.H.G. Hallei, A.D. Headley and M. Athar, *Soil Water Res*., **1**, 158 (2006).
18. G. Cekstere and A. Osvalde, *Urban For. Urban Green*., **12**, 69 (2013).
19. T. Duong and B. Lee, *Environ. Manage*., **92**, 554 (2011).
20. J. Carrero, I. Arrizabalaga, J. Bustamante, N. Goienaga, G. Arana and J.M. Madariaga, *Sci. Total Environ*., **458-460**, 427 (2013).
21. C.S. Tamrakar and P.R. Shakya, *Pak. J. Anal. Environ. Chem*., **12**, 32 (2011).
22. M. Aslam, D.K. Verma and R. Dhakerya, *Res. J. Environ. Earth Sci*., **4**, 1060 (2012).
23. M.S. El-Shahawi, A. Hamza, A.S. Bashammakh and W.T. Al-Saggaf, *Talanta*, **80**, 1587 (2010).
24. S.M. Al-Shayeb and M. Seaward, *Asian J. Chem*., **13**, 407 (2001).
25. M.S. Akhter and I.M. Madany, *Water Air Soil Pollut*., **66**, 111 (1993).
26. I. Narin, M. Soylak and M. Dogan, *Environ. Bull.*, **6**, 749 (1997).
27. D.E. Guven and G. Akinci, *GU J. Sci*., **24**, 29 (2011).
28. L. Hakanson, *Water Res*., **14**, 975 (1980).
29. K.B. Mmolawa, A.S. Likuku and G.K. Gaboutleeloe, *Afr. J. Environ. Sci. Technol*., **5**, 186 (2011).
30. G. Muller, *Geol. J.*, **2**, 108 (1969).
31. S. Budavari, M.J. O'Neil and A. Smith, the Merck Index, Merck & Co. Inc., USA, edn 13, pp. 440-462 (2001).
32. K.H. Wedepohl, *Geol. Rundschau*, **80**, 207 (1991).
33. S.A. Abbasi, P.C. Nipaney and R. Soni, *Anal. Lett*., **22**, 225 (1989).
34. M.W. Kadi, *J. Hazard. Mater*., **168**, 1280 (2009).
35. J.J. Clark and A.C. Knudsen, *J. Environ. Qual*., **42**, 1498 (2013).
36. R.A. Goyer and M.A. Mehlman, Advances in Modern Toxicology; In: Toxicology of Trace Elements. Wiley, New York, Vol. 2 (1977).
37. S. Bengtsson and G. Tyler, Vanadium in the Environment, University of London, Monitoring and Assessment Research Centre, (MARC Report No. 2), London (1976).
38. M.W. Paschke, E.F. Redente and D.B. Levy, *Environ. Toxicol. Chem*., **19**, 2751 (2000).
39. R.L. Chaney and J.A. Ryan, in eds.: H.A.J. Hoitink and H.M. Keener, Heavy Metals and Toxic Organic Pollutants in MSW-Composts: Research Results on Phytoavailability, Bioavailability, Fate *etc*. In: Science and Engineering of Composting: Design, Environmental, Microbiological and Utilization Aspects, Ohio State University, Ohio, pp. 451-506 (1993).
40. NEQS (National Environmental Quality Standards), Pakistan Environmental Legislation, Ministry of Environment (1997).