

## Assessment of Heavy Metals in Roadside Soil Samples in Zawia City, Libya

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This report is based on the assessment of four heavy metals: lead, chromium, nickel, and copper, in thirty-two roadside soil samples, one of which was a virgin soil, in Zawia City, Libya. During spring 2019, soil samples were collected from five sites along Jamal Street starting from the old university building to Al-Shuhadaa Square. The atomic absorption spectrometer Perkin Elmer AAnalyst 400 was used in this study using absorption mode, except for the use of Cu emission mode due to the unavailability of the Cu lamp. Results showed that the highest concentrations of the investigated elements were: 36 mg/kg for Pb, 15.6 mg/kg for Cr, 8.3 mg/kg for Ni, and 50 mg/kg for Cu. These values are in agreement with the allowable values of heavy metal concentration of soils in some European countries (i.e. Austria, Germany, and France). However, the concentration values for Pb, Cr, Ni, and Cu were 5.2, 2.9, 2.3, and 7.8 fold higher, respectively, than that of the virgin soil sample collected about 10 km away from the city centre. The sample preparation method used in this work was demonstrated to be suitable, showing acceptable recovery values (R%) of 94.6%, 81.9%, 87.6%, and 90.7% for Pb, Cr, Ni, and Cu, respectively.

**Key words:** Heavy metals; roadside soil; atomic & emission spectroscopy

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Zawia City is one of the highly populated Libyan cities of about 230,000 inhabitants [1], most of whom are concentrated in the city center. Zawia is situated 45 km west of the capital Tripoli. Heavy metals are well-thought-out to be among the main sources of pollution in the environment because of their significant effects on the ecological quality [2,3]. Soil is one of the critically exposed mediums to a number of pollutants due to different human activities [4]. The main sources of heavy metal pollution in the environment are man-made activities, including combustion of fossil fuels, mining activities, wastewater discharges of manufacturing industries, and waste disposal [5]. To monitor the environmental pollution, determination of heavy metals such as cadmium, lead, iron, manganese etc. in soil samples is considered to have a very important role [6,7]. Metals like iron, copper, manganese, and zinc are crucial metals as they play important roles in biological systems, whilst lead and cadmium are non-crucial metals, since they are toxic even in trace amounts [8]. However, the crucial metals can also create toxic effects at excessively elevated levels.

The presence of toxic metals in soil can rigorously obstruct the biodegradation of organic contaminants [9]. High levels of heavy metals in soil may pass to the aquatic environment, groundwater, and plants, and through the transfer processes that

reach animals, eventually humans through the food chain (soil-plant-human or soil-plant-animal-human). Poisonous effects of heavy metals have been previously studied [10-12]. Heavy metals may enter the food chain via edible plants. Therefore, determination of heavy metals in environmental samples is very imperative. Some heavy metals have considerably toxic and hazardous effects on human health. It is known that lead is a health risk metal for humans and its effects include blood enzyme changes, anemia, hyperactivity, headache, chills, diarrhea, and neurological disorders, even in low concentrations [13,14]. Similar to lead, the source of chromium is vehicle fuel. When chromium accumulates in soil and in the presence of water, it undergoes transformation into various mobile forms such as hydro chromate ( $\text{HCrO}_4^-$ ), chromate ( $\text{CrO}_4^{2-}$ ) and dichromate ( $\text{Cr}_2\text{O}_7^{2-}$ ), before ending into the environmental sink [15,16]. Although chromium toxicity in the environment is quite rare, it still offers some risks to human health as it can accumulate on skin, lungs, muscle fat, and liver, where it causes various health conditions [17].

It is also known that copper is a critical element, yet it may be toxic to both humans and animals when its concentration exceeds the safe limits. Its concentration in some human tissues such as thyroid gland can be changed depending on the tissue

state, including cancerous or non-cancerous [18]. There is a relationship between long term exposure to copper and weakening of intelligence in young adolescents [19]. The World Health Organization (WHO) reported acceptable weekly intakes of Pb as 0.025 mg/kg body weight for all human groups [20]. It is seen that this metal can seriously affect human health even at ultra-trace concentrations. Copper is strongly adsorbed to soil particles and therefore has very little mobility relative to other trace metals [21]. As a result of this limited mobility, applied copper tends to accumulate in soil [22]. Soil types have finite holding capacities for copper ions, and leaching can occur when the copper levels applied exceed this capacity [23].

Many techniques and analytical methods have been reported over the past 50 years for the determination of metal ion concentrations in different environmental samples such as water, soils, and sediments [24]. Various methods have been reported for the digestion of soil samples such as a mixture of HF-HClO<sub>4</sub> in an open digestion system [25] and mixture of HCl/HNO<sub>3</sub> [4]. Whilst digestion using both open digestion and microwave techniques has been reported [2], Tuzen *et al.* [6] used a mixture of aqua regia and perchloric acid solution. Bentum *et al.* used a tertiary acid mixture of perchloric acid: sulphuric acid; nitric acid for soil digestion [26], whilst H. Isen *et al.* used a more complicated sequential extraction method for soil examples using acetic acid, hydroxylamine hydrochloride, hydrochloric acid, hydrogen peroxide, ammonium acetate, and aqua regia [27]. In this work, the digestion has been done in a closed system using a mixture of HCl and HNO<sub>3</sub> solutions at about the boiling point of water.

## EXPERIMENTAL

### Reagents

Chemicals used were of analytical grade reagents. Hydrochloric acid was from Riedel de-Haen and nitric acid was from Timstra Laboratory Supplier Ltd. Distilled water was supplied from Zawia electric station.

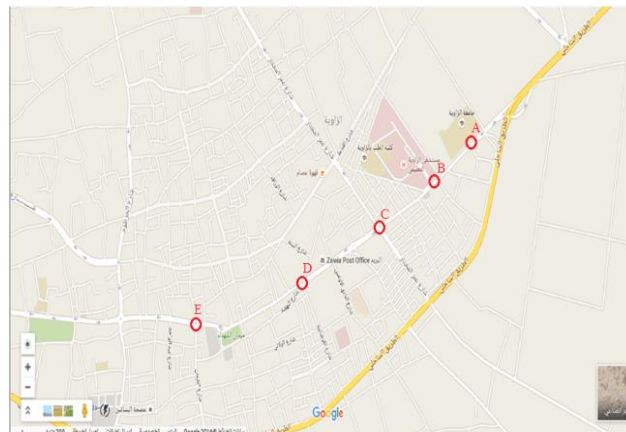
### Sampling and Sample Preparation

This study was based on the investigation of the environmental pollution in Zawia City. Thirty-two (32) samples were collected along the main road (i. e., Jamal Street), starting from the old university building to Al-Shuhadaa Square roundabout as shown in Figure 1 and Table 1.

**Table 1.** Samples identifications

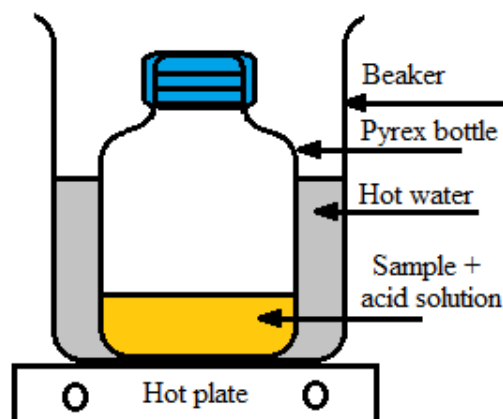
Site code	Location	Number of samples
A	The old university	3
B	Zawia Hospital	5
C	Raihana roundabout	13

D	Military station roundabout	6
E	Al-Shuhadaa square roundabout	4
F	Virgin land sample	1



**Figure 1.** Part of Zawia City map representing the sampling locations

However, from every location, surface samples were taken in addition to samples taken from different depths (i.e., 5, 10, and 15 cm) in certain locations, as stated later. The samples were dried at room temperature for 24 hours, hand ground, and kept in plastic bags. Accurately  $3.0 \pm 0.001$  g of each sample was weighed into a 50 ml pyrex container provided with a tight screw lid (Fig. 2). 13.5 ml of HCl/HNO<sub>3</sub> (3:1) mixture was then added to each container. The containers were tightly closed and heated in a water bath for 2 hrs at about 95°C. The mixtures were cooled to room temperature and filtered through Whatman filter paper N0. 40, with the filtrates received in 100 ml volumetric flasks. The remaining residues were washed three times with 3 portions of 10 ml of distilled water, adding the washings to the main filtrates. The volume was made up to the mark with distilled water. The solutions were properly shaken and immediately transferred to polypropylene storage bottles and analyzed with atomic absorption spectroscopy.



**Figure 2.** Apparatus for sample digestion

A certified standard material was analyzed as reference to the method. The reference sample used in this system was stream sediment (SARM 51) and used as received without any treatment. On the other hand, one sample from a virgin agricultural area about 10 km away from the city centre was collected and treated as a comparable sample. Three replicates for each sample and a blank solution were prepared in the same way. The standard solutions were re-measured after running every ten to fifteen samples, and the instrument was recalibrated as required.

An atomic absorption spectrometer Perkin Elmer A Analyst 400 was used for the determination of the elements with working conditions as summarized in Table 2. A series of standard solutions for each element were prepared and measured, resulting in the calibration curves as shown in Figure 3 with determination coefficients higher than 0.999. All elements were measured at absorption mode, except Cu which was measured by emission mode due to the unavailability of its hollow cathode lamp. Perkin Elmer AAS Software has the ability to create linear and non-linear through zero calibration curves. For the former, equation 1 was used to calculate the concentration (C), whilst equation 2 was used for the latter [28].

$$C = K_0(-K_1A) \quad (\text{Eqn.1})$$

$$C = K_0 \frac{K_1A + K_3A^2}{K_2A - 1} \quad (\text{Eqn.2})$$

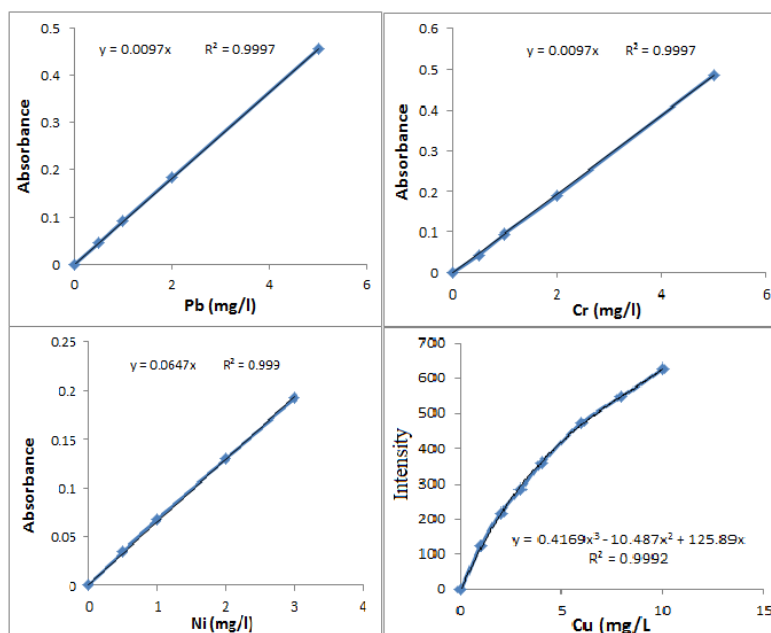
Where,  $K_0$  is re-slope coefficient which fits to 1.0, and  $K_1$ ,  $K_2$ , and  $K_3$  are coefficients calculated during calibration.

**Table 2.** Instrumental working conditions for Pb, Ni, Cr and Cu.

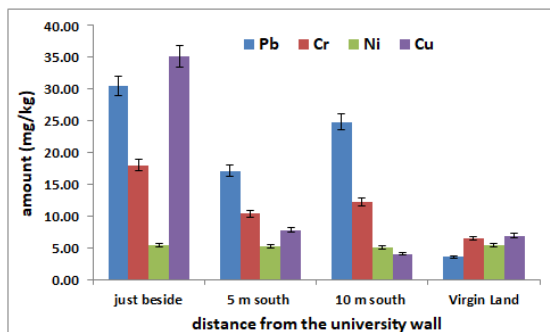
Parameters	Pb	Ni	Cr	Cu
Lamp current (mA)	12	25	10	emission
Wavelength (nm)	283.3	231.6	257.9	327.4
Slit (nm)	0.7	0.2	0.7	0.2
Burner height (mm)	10	10	10	10
Acetylene flow rate (L/min)	2.5	2.5	2.5	2.5
Air flow rate (L/min)	10.0	10.0	10.0	10.0

### RESULTS AND DISCUSSION

From the results obtained, it was shown that the concentration of metal ions was higher at the wall of the university, which is about 10 meters far from the road (Figure 4). The concentration decreased as we go further from the university wall up to 5 meters. At the main road, the concentration increased again. To explain this, one could say that due to dust movement by wind, the metal ions accumulate beside the wall and remain, as not many people walking there. At the main road, the concentration was high especially for  $Pb^{2+}$  and  $Cr^{3+}$ , which may be attributed to transportation contribution. At the middle distance between the road and the university wall, the



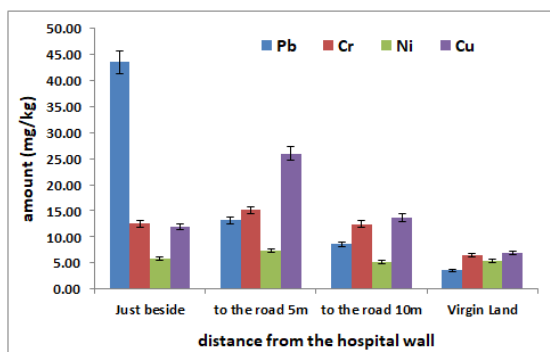
**Figure 3.** Calibration curves for Pb, Cr, Ni, and Cu



**Figure 4.** Distributions of metal ions at the old university

concentration of  $Pb^{2+}$  and  $Cr^{3+}$  was at about half the amount of that at the university wall, as this area is mostly the human-crowded area and this could affect the concentration. The concentration of  $Cu^{2+}$  at the main road and at about 5 meters from the wall was almost similar to that of the sample taken from the virgin soil, which one could say it was just at the natural level. Whilst, the concentration of  $Ni^{2+}$  did not show any differences at all distances compared to that of the virgin soil. This means there was no contribution of traffic in case of  $Ni^{2+}$  as well. Whereas, at the wall,  $Pb^{2+}$  showed up to 10 fold higher than that of the virgin soil sample. For  $Cu^{2+}$ , it was about 5 times higher. For  $Cr^{3+}$ , it was 3 times higher than the virgin area.

In the hospital area,  $Pb^{2+}$  showed the highest concentration beside the wall and decreased 12, 4, and 2 fold of the virgin land sample as the distance increased, as shown in Figure 5. Whilst  $Cu^{2+}$  and  $Cr^{3+}$  were highest at 5 m distance to the road, 4 and 2 fold of the virgin land sample, respectively. Whereas, no significant change was observed beside the wall and 10 m to the road for  $Cu^{2+}$  and  $Cr^{3+}$  where the concentration was 1.7 and 1.98, and 1.95 and 1.93 fold of the virgin land sample, respectively.

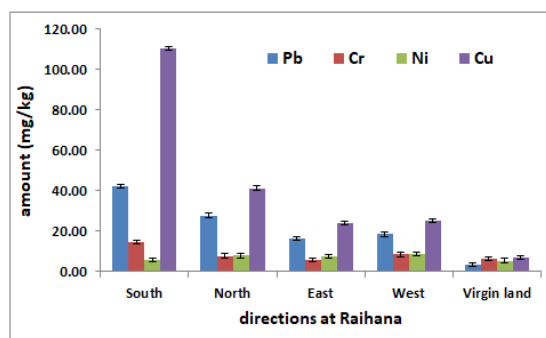


**Figure 5.** Distributions of metal ions at the hospital

Figure 6 shows the distribution of metal ions at the Raihana roundabout. Based on Figure 6,  $Pb^{2+}$  showed the highest concentration in all directions compare to

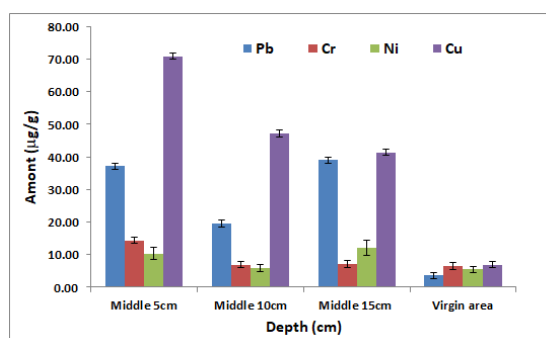
$Cu^{2+}$  and  $Cr^{3+}$ . In the south direction,  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cr^{3+}$  were the highest.  $Pb^{2+}$  and  $Cu^{2+}$  showed the same trend, concentration decreased in the following order: south > north > east > west. Whereas,  $Cr^{3+}$  showed the following trend: south > west > north > east.

The average of  $Pb^{2+}$  was about  $26 \pm 12$  mg/kg,  $Cr^{3+}$  was about  $9 \pm 4$  mg/kg,  $Ni^{2+}$  was  $7.5 \pm 1.2$  mg/kg, and  $Cu^{2+}$  was very high in the south direction (110 mg/kg), whilst the average in the other directions was  $30 \pm 10$  mg/kg. These values were higher than those for the virgin land sample of about 7.3, 1.4, 1.4, and 7.3 times for  $Pb^{2+}$ ,  $Cr^{3+}$ ,  $Ni^{2+}$ , and  $Cu^{2+}$ , respectively.



**Figure 6.** Metal ion concentrations in the surface soil at different directions of the Raihana roundabout

Figure 7 shows the data for samples taken from the military station roundabout at different depths of 5, 10, and 15 cm and from the surface. Here we could see that  $Cr^{3+}$  and  $Cu^{2+}$  concentrations decreased with increasing depth from 5 to 15 cm. Whereas,  $Pd^{2+}$  and  $Ni^{2+}$  showed lower concentrations at the depth of 10 cm than 5 and 15 cm. Compared to the virgin land sample, we could see that the concentration at the depth of 5 cm was 10.4 times higher for  $Pb^{2+}$ , 2.2 times higher for  $Cr^{3+}$ , 1.9 times higher for  $Ni^{2+}$ , and 10.3 times higher for  $Cu^{2+}$ .



**Figure 7.** Depth effect on metal ion concentrations at the military station roundabout

Figure 8 shows that the average concentrations of the elements in the Al-shuhadaa Square was about  $47 \pm 8$  mg/kg for  $Cu^{2+}$ ,  $37 \pm 3.6$  mg/kg for  $Pb^{2+}$ ,  $11 \pm 6$  mg/kg for  $Cr^{3+}$ , and  $5.4 \pm 1$  mg/kg for  $Ni^{2+}$ . These values were about 7, 10, 2, and 1 times of that of the virgin land

sample for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Ni}^{2+}$ , respectively. Allowable limits of some heavy metals in some European countries are shown in Table 3.

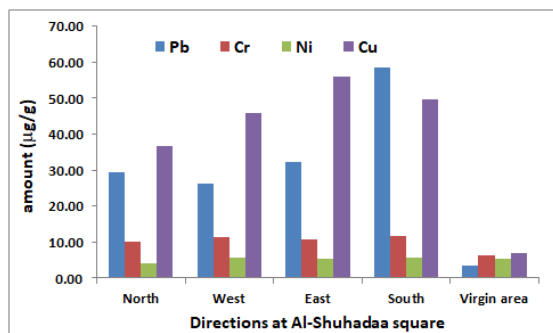


Figure 8. Metal ion concentrations at different directions of the Al-Shuhadaa Square

Table 3. Allowable limits of some heavy metals in soil (mg/kg) in Europe [29]

	Cr	Cu	Ni	Pb
Austria	100	60-100	50-70	100
Germany	60	40	50	100
France	150	100	50	100
Luxembourg	100-200	50-140	30-75	50-300
Holland	30	40	30	40
Sweden	60	40	30	40
UK	400	135	75	300

Source: ECDGE (2010)

As shown in Figure 9, the average values of the elements in the studied sites were in agreement with the allowable concentrations in most European countries, as shown in Table 3. The highest concentration of Pb was 36.6 mg/kg in the Al-Shuhadaa Square, whilst the highest concentration of  $\text{Cu}^{2+}$  was 50 mg/kg in the Raihana roundabout, the other two elements very acceptable.

It is also clear from Figure 9 that the concentration of  $\text{Pb}^{2+}$  increased as we go from east to west. Whereas,  $\text{Cu}^{2+}$  showed a different non-uniform trend exhibiting two values, one was about 15 mg/kg at the east side and the second was about 45 mg/kg at the west side.  $\text{Cr}^{3+}$  and  $\text{Ni}^{2+}$  did not show any significant differences.

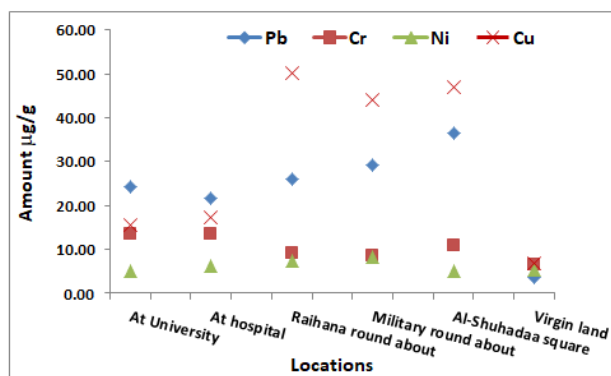


Figure 9. General overview of the metal ion concentrations compared with the virgin land sample

## RECOMMENDATIONS

Although the concentrations of the studied elements were acceptable according to the data in Table 3, it could be recommended that there should be extensive awareness campaign on the need for the improvement of fuel quality and the placement of emission standards to reduce the impact of vehicle emissions. More investigative studies on other toxic elements are also required to assess the overall pollution in the city.

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