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Determination of Aerosol Metals Pollutants in Falling Dust in Benghazi City, Libya

Sami H Almabrok*, Mussa M Ali, Yasmin Y Mohammed, and Eman N Zew

Department of Chemistry, Faculty of Science, University of Benghazi, Benghazi, Libya

Abstract

The aim of this study is to determine the levels of concentrations of selected heavy metals of aerosol metals contamination in falling dust at different roadsides in Benghazi city. In order to do that, measuring the concentrations of the selected aerosol metals by using vacuum pump and measured using atomic absorption spectroscopy (AAS) technique. Six composite samples were collected along roadsides and each sample was represented average of five samples which collected from that particular area. The concentrations of aerosol metals of each site were based on density of traffic road and type of industrial activities, also to the number of population. Each measured sample was replicated three times to obtain representative and accurate values. Also, a statistical analysis including mean and standard deviation were carried out. Correlation coefficient of calibration curves of measured aerosol metals was shown a good response, where the R^2 value was ranged between 0.994 to 0.999. The range of concentrations of the studied aerosol metals were varied as following: Cobalt (90-344 mg/kg), iron (120-383 mg/kg), lead (153-740 mg/kg), zinc (78-468.7 mg/kg), copper (80-180 mg/kg), selenium (40-133 mg/kg), cadmium (90344 mg/kg), potassium (318-2932 mg/kg), sodium (587.5-3006 mg/kg), calcium (286.6-1185.7 mg/kg) and magnesium (65-325.8 mg/kg). A significant positive correlation was shown between each pairs of measured elements Pb/Zn, Pb/Co, Pb/Cu, Pb/Se, Zn/Co and Zn/Cu.

Keywords: Aerosol metals • Sampling sites • Street dust • Dust • Atomic absorption spectroscopy

Introduction

The Earth's atmosphere is defined as the gaseous envelope surrounding the planet and it plays an important role in the transfer of energy between the Sun and the planet's surface; this process maintains the thermal equilibrium that supplies a suitable temperature range to the Earth. The Earth's atmospheric chemistry is directly related to oceans and surface processes; therefore, the oceans, the surface processes, and the atmosphere are especially important components for life [1]. Particulate matter is defined as a suspension of fine solid or liquid particles in the gas phase. The main sources of particulate matter in the atmosphere are natural and anthropogenic emissions; natural sources include windborne dust, sea spray and volcanoes; anthropogenic activities include combustion of fuels [2]. Tropospheric aerosol contains sulfate, ammonium nitrate, sodium, chloride, trace elements, carbonaceous material and water. Carbonaceous material includes elemental carbon and organic carbon. The elemental carbon is called black carbon, graphite carbon, or soot and is directly emitted into the troposphere from the combustion of fuels. The organic carbon is directly emitted or formed by condensation of low volatility organic gases. Anthropogenic emissions have increased dramatically over the past century, this increase has affected human health, reduced visibility in urban regional areas, and this led to acid deposition, impacted on the Earth's radiation balance. The visibility is reduced, when the light from the Sun is absorbed and scattered by the particles between the observer and the object, this decreases the contrast between the object and background sky and the consequence is to reduced visibility [2].

Dust is classified as a type of aerosol in air pollution with diameters less than 500 micrometers. Dust aerosols can be formed from different sources such assoil dust by wind as air pollution. However, dust encompasses minor amounts of many materials which may be found in the local atmosphere [3]. Street dust does not remain deposited in place for a long time. This is due to the movement of vehicles and human activity can back into the atmosphere, where it contributes a significant amount of trace elements. There are two main sources of street dus: deposition of previously suspended particles (atmospheric aerosols) and displaced soil. Heavy metals release in atmospheric particles maybe cause problem to ecosystem and side effect on the human being due to accumulation factor. This might be via inhalation or respiratory deposition. Toxic heavy metals such as *arsenic,* cadmium and lead in the atmosphere cause potential hazard. For this reason, WHO has given guidelines for these elements, which are presented in air and above the natural acceptable levels due to the anthropogenic activities? Aerosols and hydrometeors are identified and characterized by their size distribution and composition. The number density of aerosol particles decreases with increasing particle size; the number density of hydrometeor particles is less than that of aerosol particles, but the mass loading of hydrometeor particles is greater than those of aerosol particles.

The aerosol particles can be divided into three categories: The nucleation mode contains particles with diameters less than 0.1 μm, these particles increase in size by coagulation and growth; only a few gases, such as sulfuric acid, water and some organic gases condense onto particles. The accumulation mode, when particles coagulate and grow to diameters between 0.1-2 μm, they are termed accumulation mode particles. Some of these particles are removed by rain, but they are still too light to be removed by sedimentation. The accumulation mode maybe sub-divided into sub-modes with diameters between 0.2 μm and 0.5 to 0.7 μm. Accumulation mode particles are important for two reasons. First they affect health by penetrating into lungs. The second effect is visibility. The particles in

***Address for Correspondence:** Sami H Almabrok, Department of Chemistry, Faculty of Science, University of Benghazi, Benghazi, Libya, Tel +00218911638288; E-mail: sami.almabrok@uob.edu.ly, sami.hus2009@googlemaill.com*

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nucleation and accumulation modes are called fine particles. The coarse mode consists of particles larger than 2μm in diameter, these particles originate from windblown dust, sea spray, volcanoes, and plants; these particles are heavy enough to sediment [4].

Our respiratory system is efficient at removing aerosols, but if these aerosols fall within particular size ranges they are considered as highly concentrated, or toxic and may cause adverse health effects. They may also deposit on skin or eyes, generally, causing irritation, though more toxic effects may occur. Very small particles may pass through the skin and enter the body that way. Soluble particles may dissolve and pass through the skin. Suspended particulate with smaller sizes can absorb heavy metals and leads to tissue damage if penetrates lungs. The health effects of suspended toxic heavy metals on the human being might be become very dangerous when an active person typically inhales between 10,000 to 20,000 liters of air per day [5]. During inhalation, these fine suspended heavy metals can enter the lungs and also blood stream. However, several other organs can be affected than the lungs. It has been estimated that a man can live weeks without food and five days without water, but only five minutes without air [5]. Heavy metals become one of the major concern over the world, which is grown over years. Contamination by dust containing heavy metals could be ended by settling in soil and find their way to reach plants, animals and humans beings. Heavy metals by accumulation factor threats human health, plant growing and animals life.

Experimental Work

Chemical and reagents

All the reagents and materials were used at high purity (≥ 95%); these materials have been ordered from Sigma-Aldrich. Pure nitric acid (99%), hydrochloric acid (99%) and hydrogen peroxide (used as digestion) were supplied by BOC.

Atomic absorption spectroscopy (AAS)

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption is a very sensitive technique that it can measure down to parts per billion of a gram in a sample. The technique is used of the wavelengths of light specifically absorbed by an element which is correspond to the energies needed to promote electrons from one energy level to another higher energy level. In AAS, the sample is atomized and converted into the ground state as free atoms in the vapor state. The beam of electromagnetic radiation emitted from excited metal atoms is passed through the vaporized sample. Some of the radiation is absorbed by the metal atoms in the sample [6].

Sampling

Random a strategy method was used to collect all the samples and six composite samples (each one representative five samples, which was covered all that particular area) from different areas in Benghazi city. This is to determine falling dust containing aerosols metals along the major roadsides. At least three replicate samples were collected from each sampling site. Roadsides falling dust samples were taken under very accurate and precise procedure to avoid any contamination or loss of the studied samples. Samples were collected from Jamal Abdul Nasser street, Al kuwafyah roadside, Venesah street, Garyuonis roadside, Tripoli roadside and Al Gawarishah. Map shown in Figure 1 illustrates where the samples were taken from in Benghazi city.

Figure 1. Map illustrating the sampling sites in Benghazi city.

Sampling collection

Samples were collected using vacuum pump. Figure 2 shown the filter paper was connected with pressure regulator and vacuum pump to determine the rate of collecting falling dust. The volume of collected falling dust samples containing aerosols metals was obtained from flow meter readings and sampling time where the flow rate was 25 to 70 CFM (Cubic feet of falling dust per minute) through the filter medium. This was running for 12 hours from 7 am to 7 pm in different places using filter papers fixed properly in glass plate. Collected dust aerosols metals were stored at room temperature after being placed in a plastic bag to avoid any contamination from surrounded atmosphere.

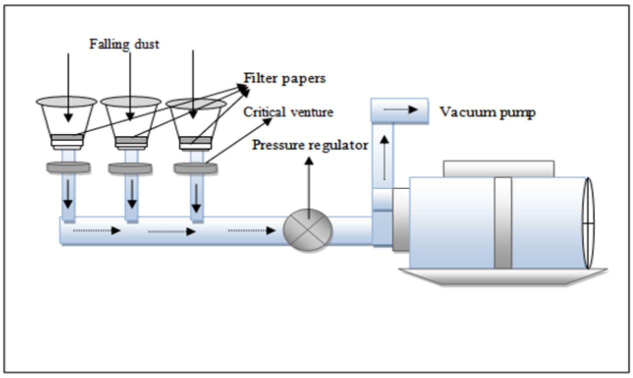

Figure 2. Schematic of collected falling dust using vacuum pump system.

Sample preparation

Falling dust samples were collected using cellulose filter membrane pore size 0.22 μm, diameter 0.47 mm. The net weight of collected dust samples (range between 0.1 g-0.2 g). All the samples were dried at 100-110°C; this to drive out moisture. Samples were kept in a petri dish to prevent any contamination. Filter paper including falling dust was placed in 50 ml beaker and then 10 ml of concentrated highly pure of nitric acid was added to the samples. The samples were heated slowly to digest; this was carried out until the amount of 10 ml of concentrated nitric acid containing sample was reduced between 2 to 3 ml due to the evaporation and then 5 ml of concentrated nitric acid was added to the sample and heated again. This step was repeated more than one time to insure the digestion of sample was completely achieved. The final extracts were filtered into a 100 ml polyethylene volumetric flask through 0.45 mm filters and then diluted to 100 using distilled water.

Standard calibration curves

All calibration curves for the studied metals (Figures 3a-3j) have shown a good response and reproducibility. Correlation coefficients for areole metals was ranged between 0.959 to 0.999.

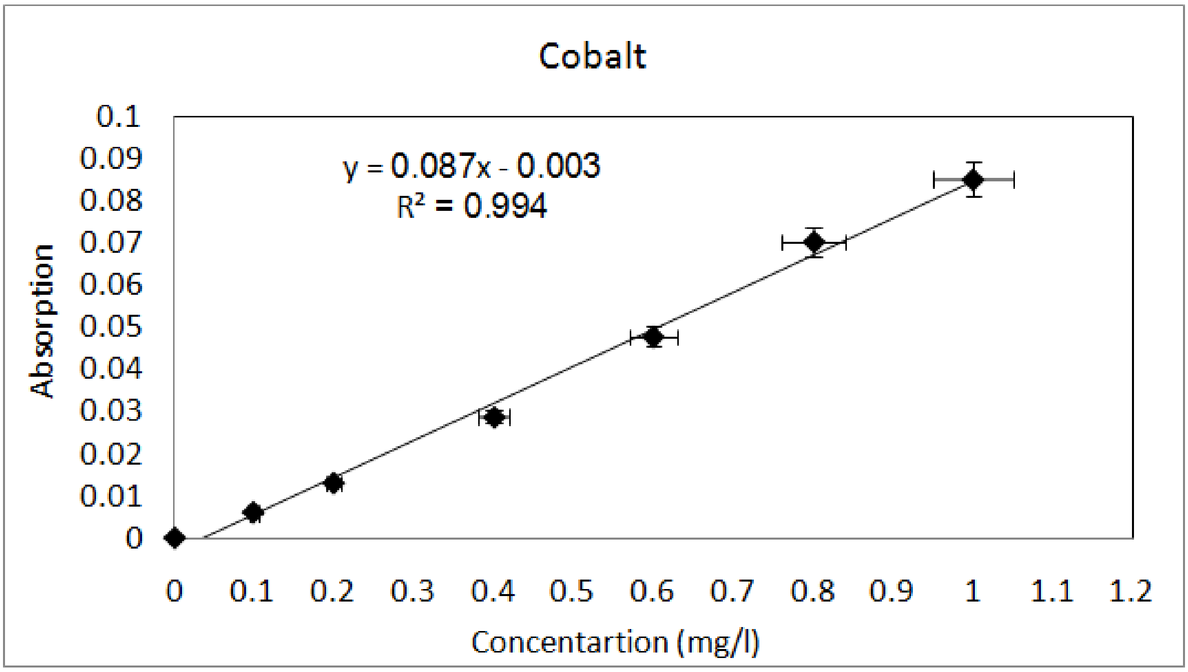

Figure 3a. Calibration curve for Cobalt.

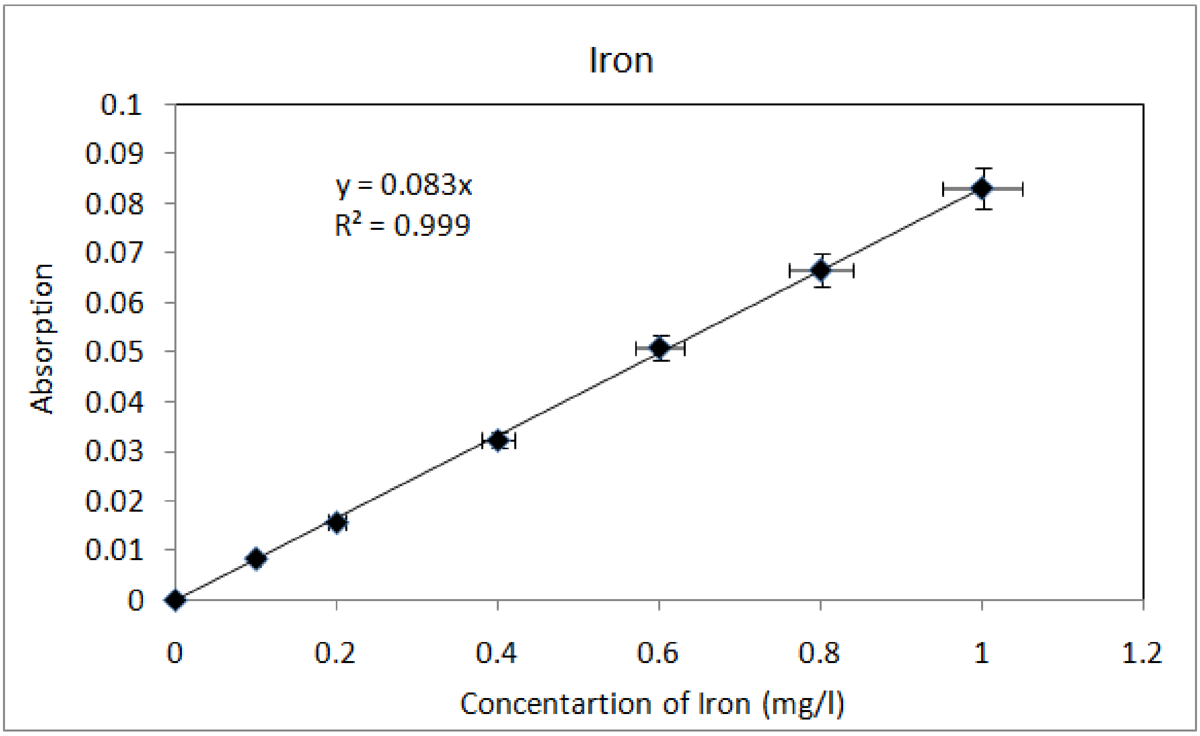

Figure 3b. Calibration curve for Iron.

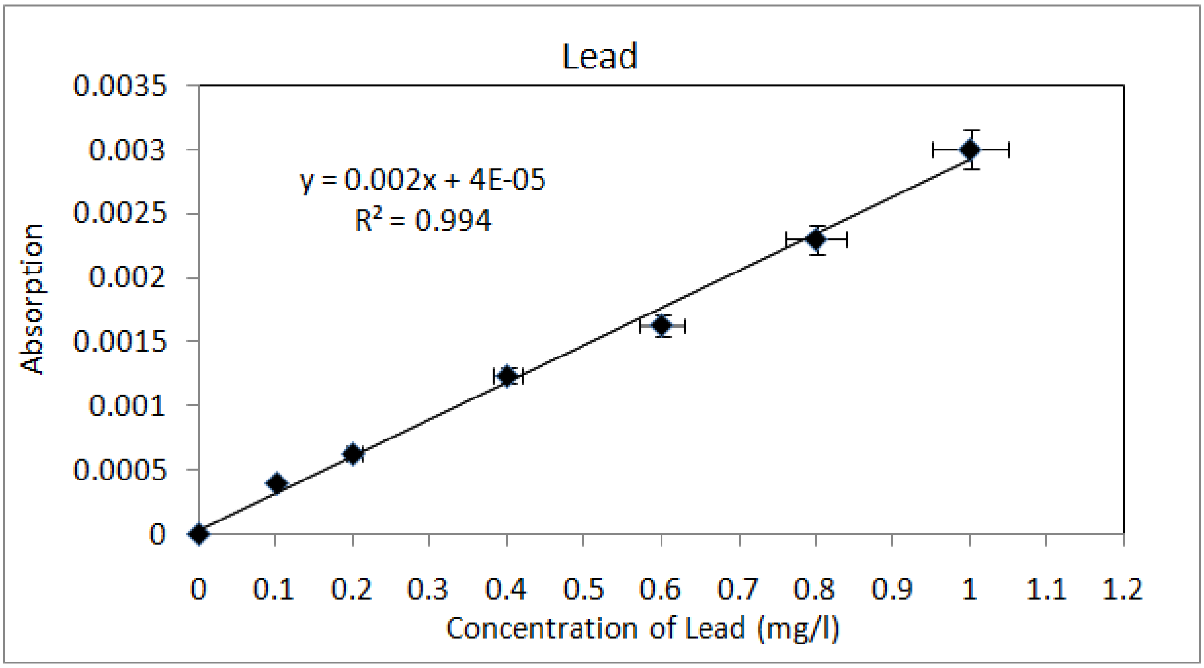

Figure 3c. Calibration curve for Lead.

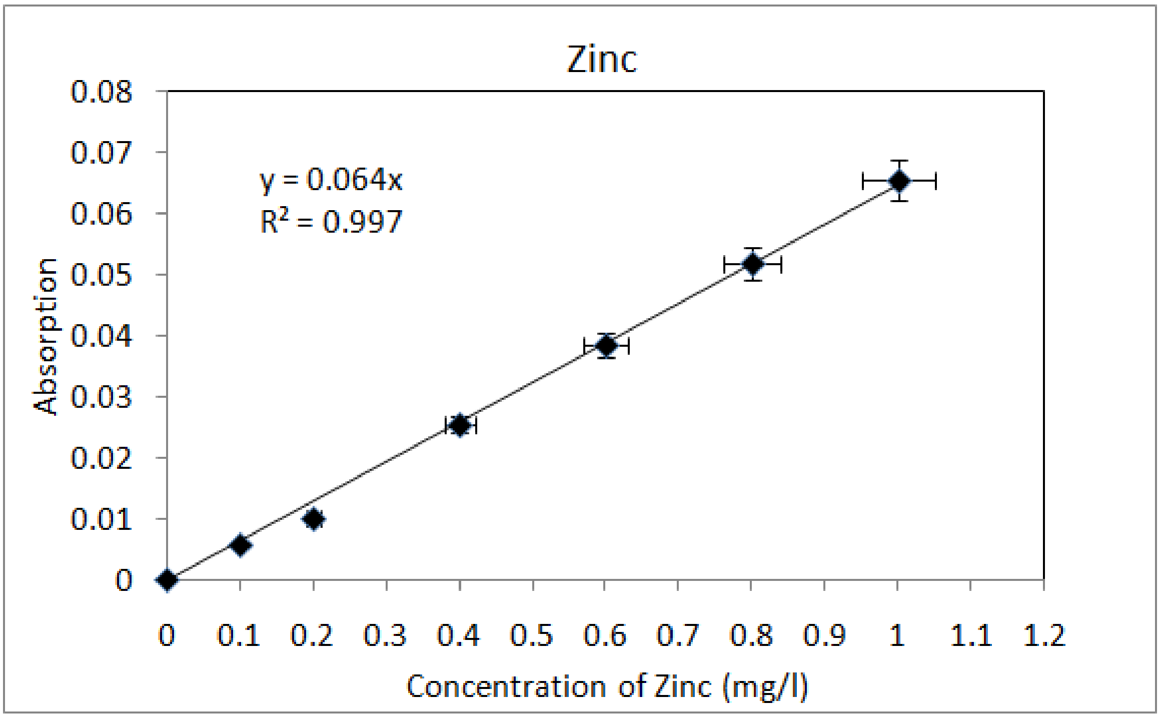

Figure 3d. Calibration curve for Zinc.

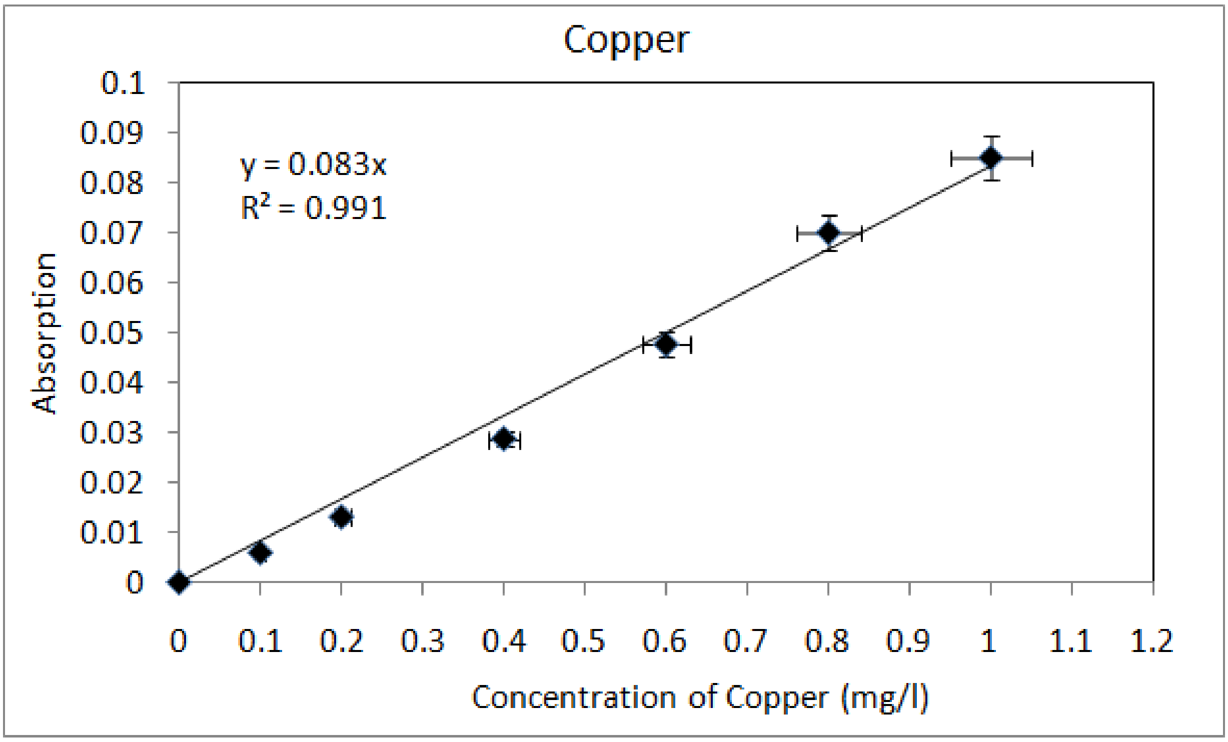

Figure 3e. Calibration curve for Copper.

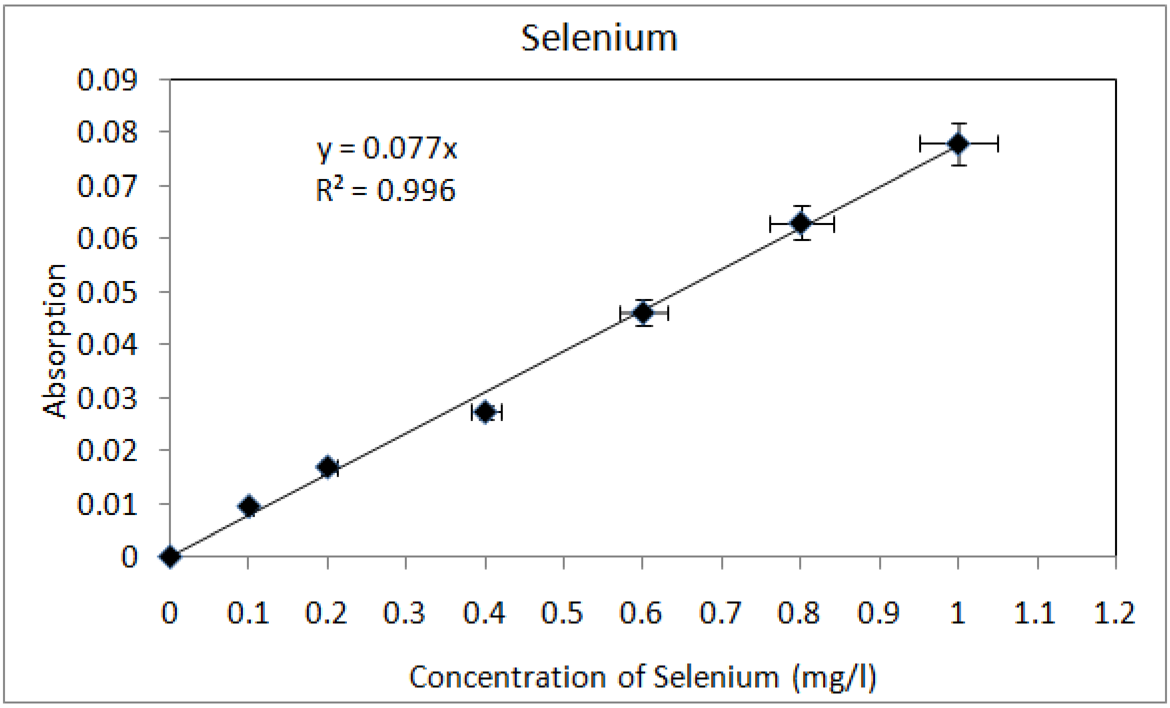

Figure 3f. Calibration curve for Selenium.

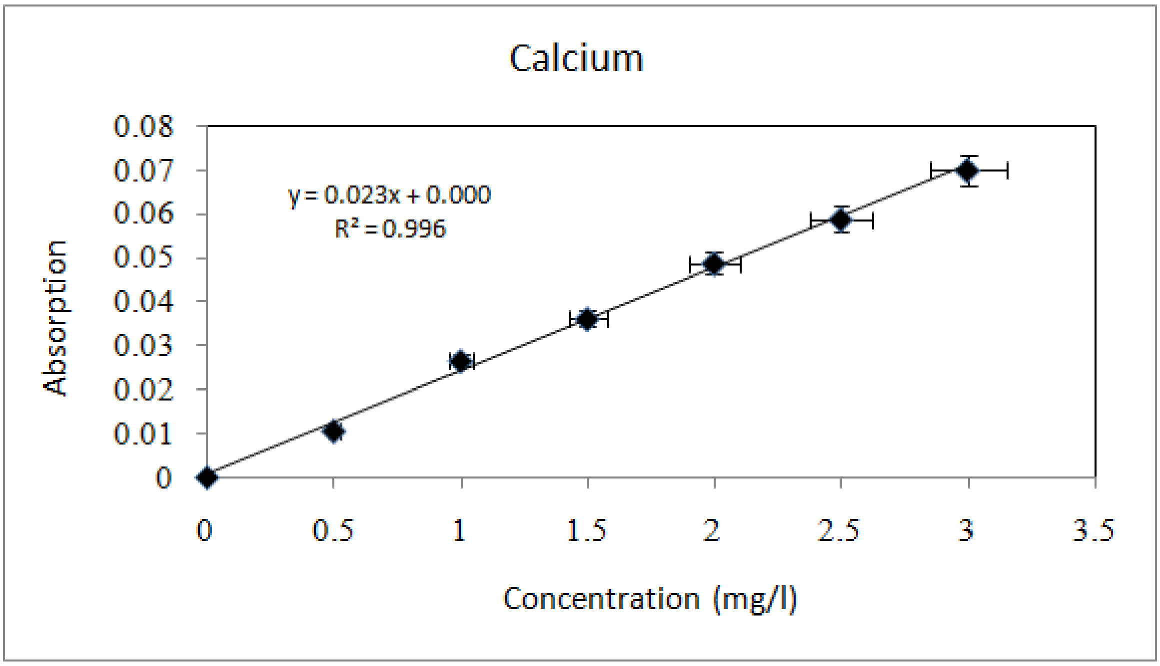

Figure 3g. Calibration curve for Calcium.

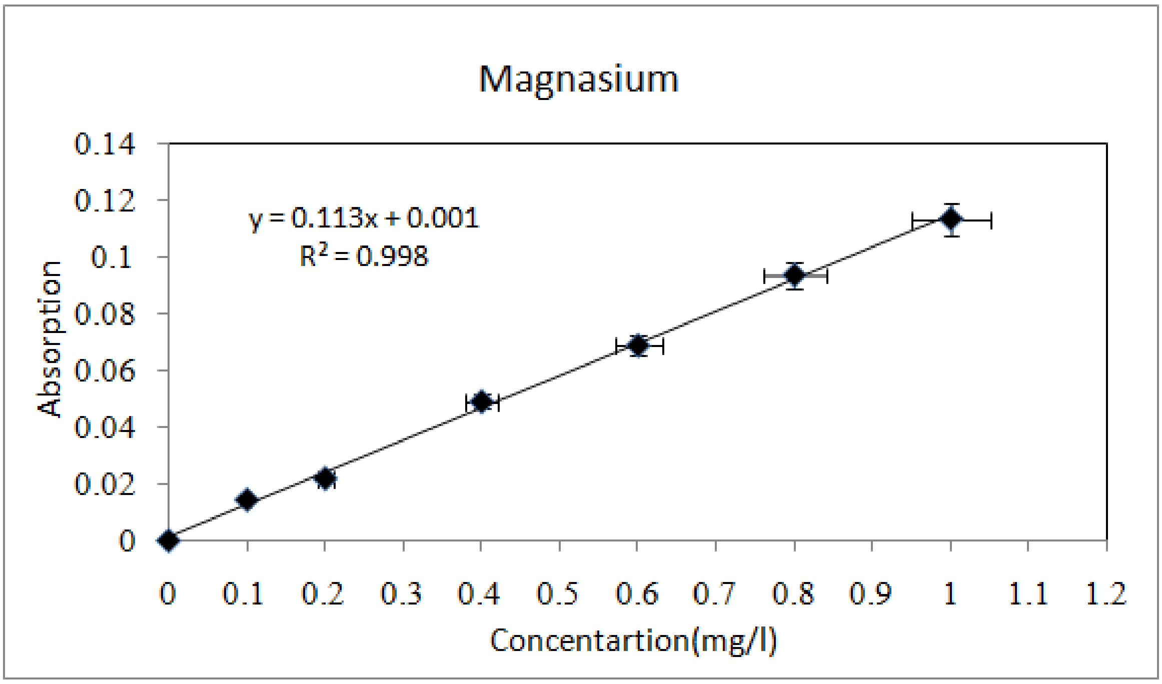

Figure 3h. Calibration curve for Magnesium.

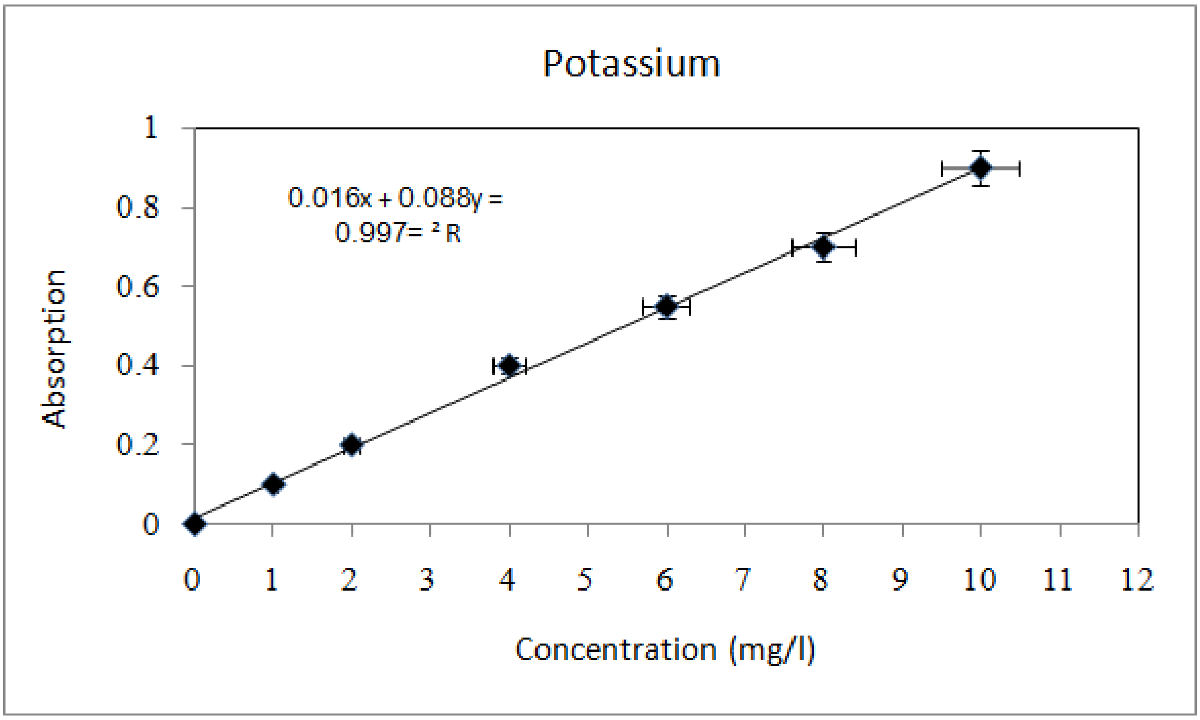

Figure 3i. Calibration curve for Potassium.

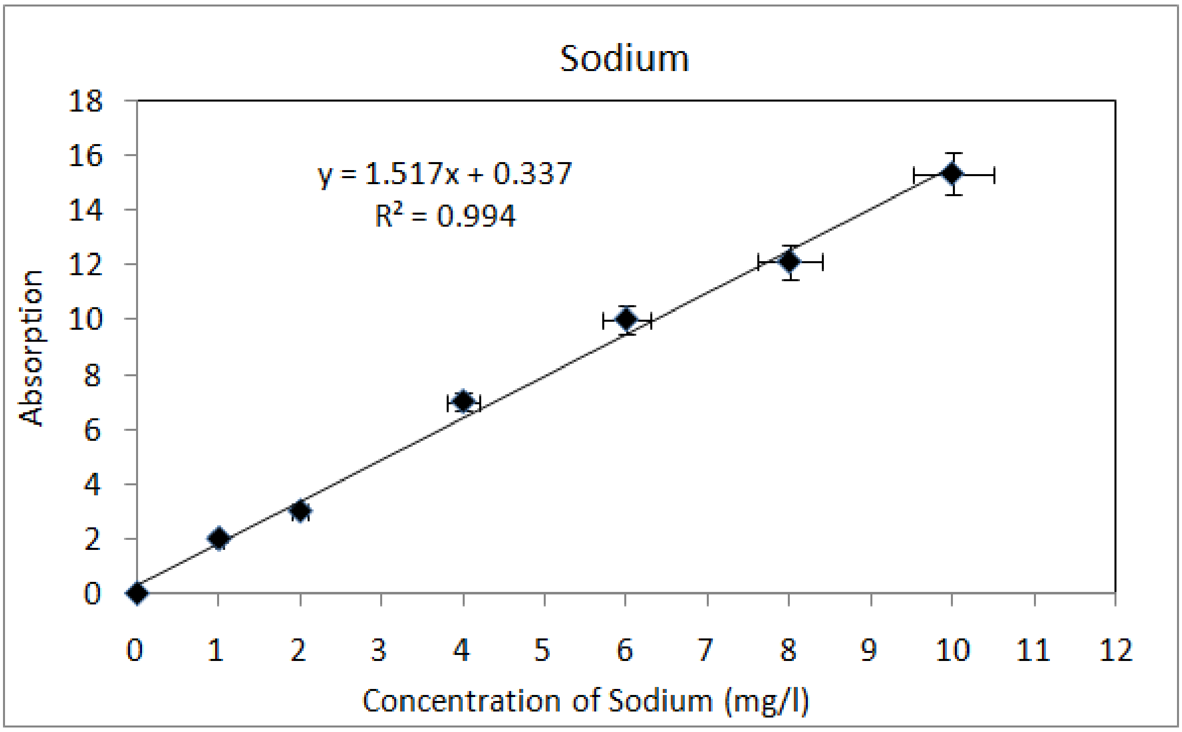

Figure 3j. Calibration curve for Sodium.

Results and Discussion

Particulate matter (PM) samples of falling dust containing metals in Benghazi city were analyzed to determine the concentrations of Co, Fe, Pd, Zn, Cu, Se, K, Na, Ca, and Mg. The result obtained for selected metals can be illustrated in Figures 4a-4j. As shown in Figure 4, the concentrations of falling dust containing metals were varied from location to location.

Concentrations of cobalt were ranged between 90 to 344 mg/kg, concentrations of iron were ranged between 120.5 to 383.4 mg/kg, concentrations of lead were ranged between 153 to 740 mg/kg, concentrations of zinc were ranged between 78.1 to 468.7 mg/kg, concentrations of copper was ranged between 80.3 to 219 mg/kg, concentrations of selenium were ranged between 40 to 133 mg/kg, concentrations of potassium were ranged between 873.3 to 3181 mg/kg, concentrations of sodium were ranged between 587.6 to 3006 mg/kg, concentrations of calcium were ranged between 286.6 to 1185.7 mg/kg, concentrations of magnesium were ranged between 64.9 to 325.8 mg/kg.

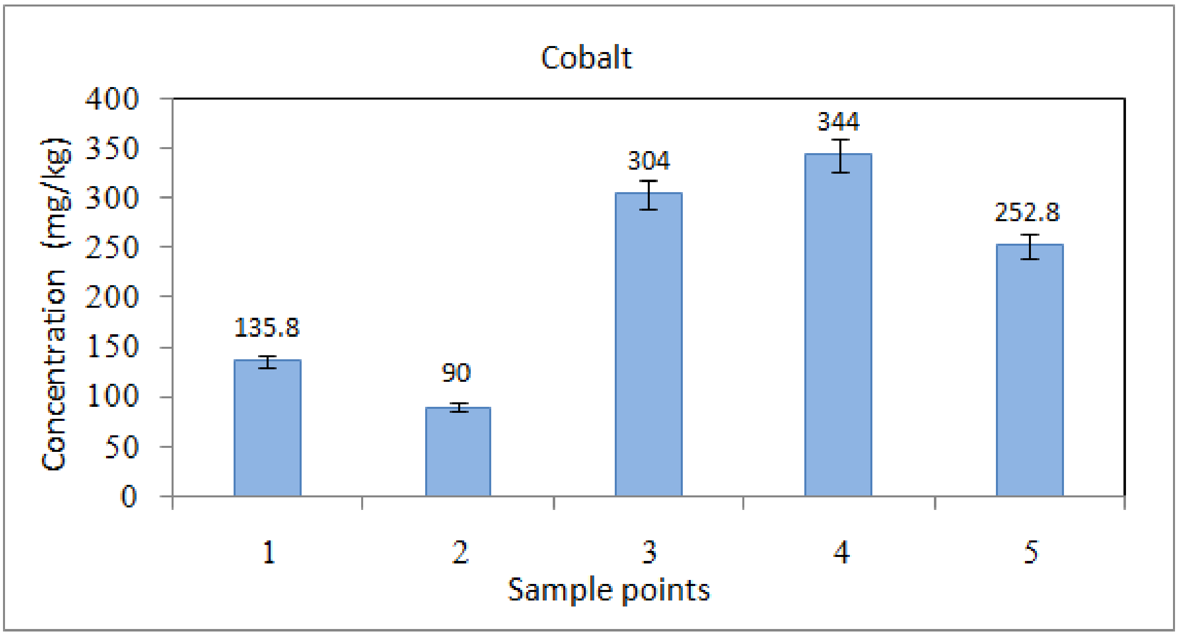

Figure 4a. Cobalt concentrations in falling dust sample.

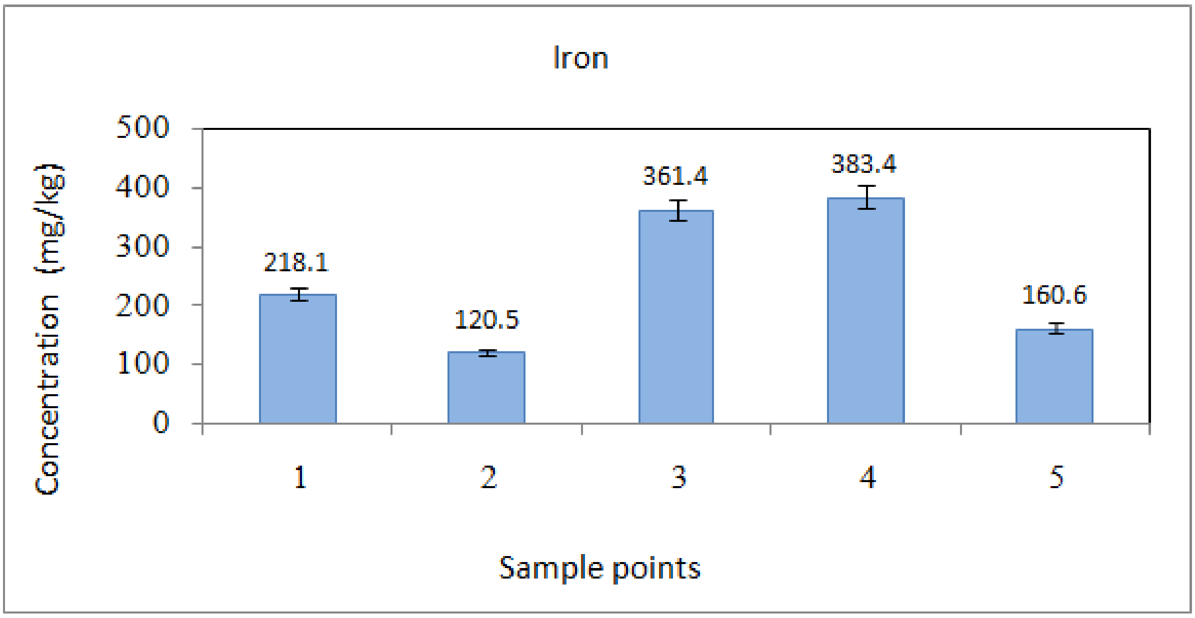

Figure 4b. Iron concentrations in falling dust sample.

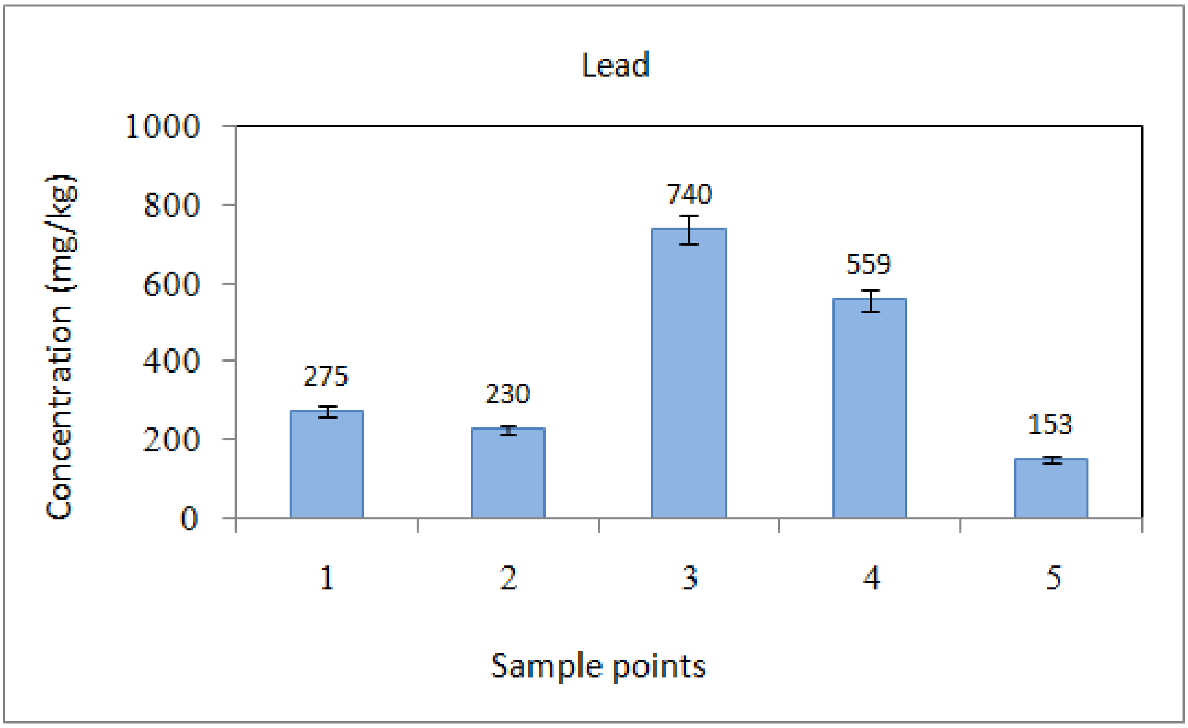

Figure 4c. Lead concentrations in falling dust sample.

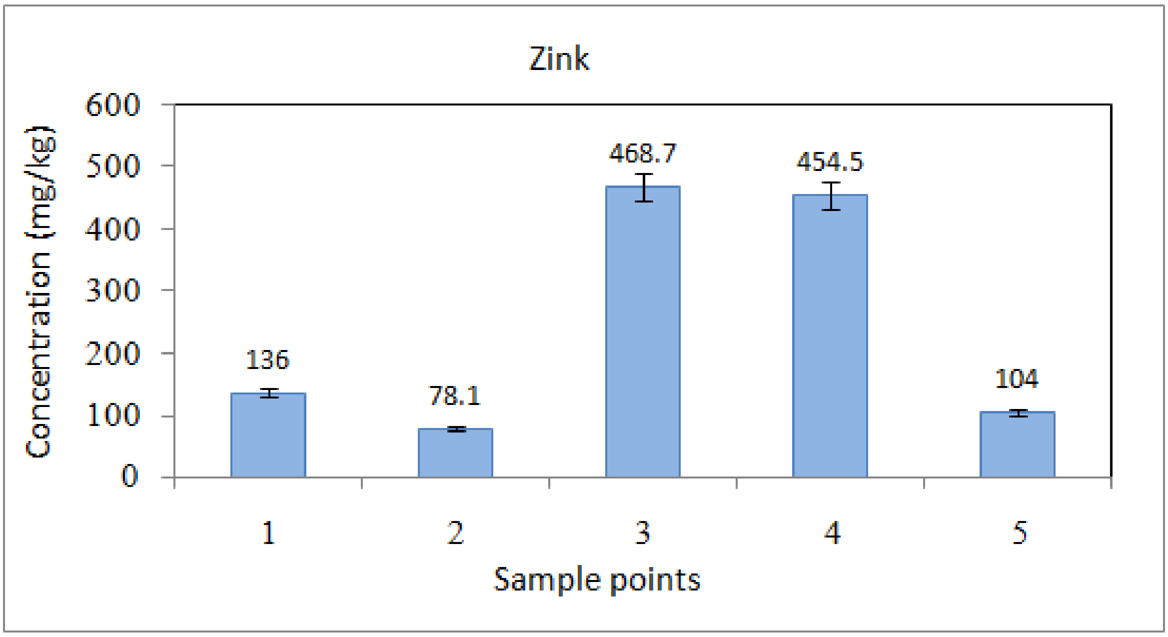

Figure 4d. Zinc concentrations in falling dust sample.

Garyuonis roadside and Tripoli roadside has shown the largest values for all the falling dust of measured elements. The reason for that, it might be referred to the industrial activities in these areas. Also, the traffic density in these areas an important factor to increase the concentrations of the measured elements in falling dust. Figures 5a-5f is shown a significant positive correlation between each pairs of measured element Pb/Zn, Pb/Co, Pb/Cu, Pb/Se, Zn/Co and Zn/Cu [7,8].

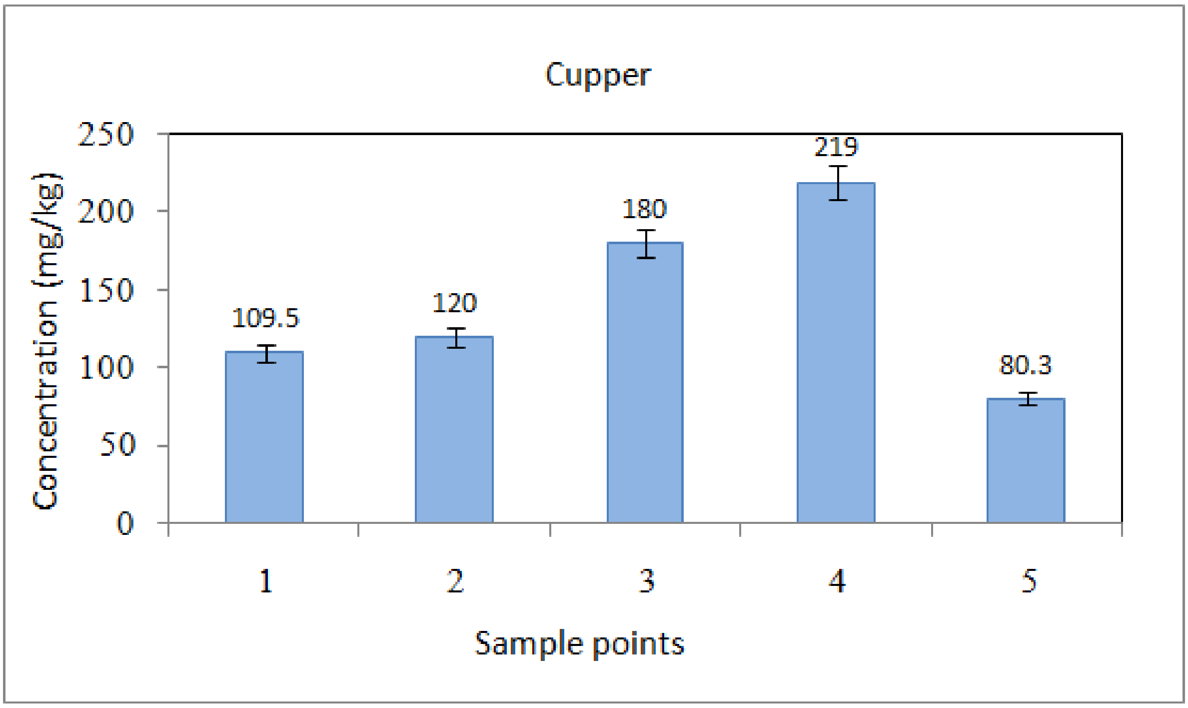

Figure 4e. Cupper concentrations in falling dust samples.

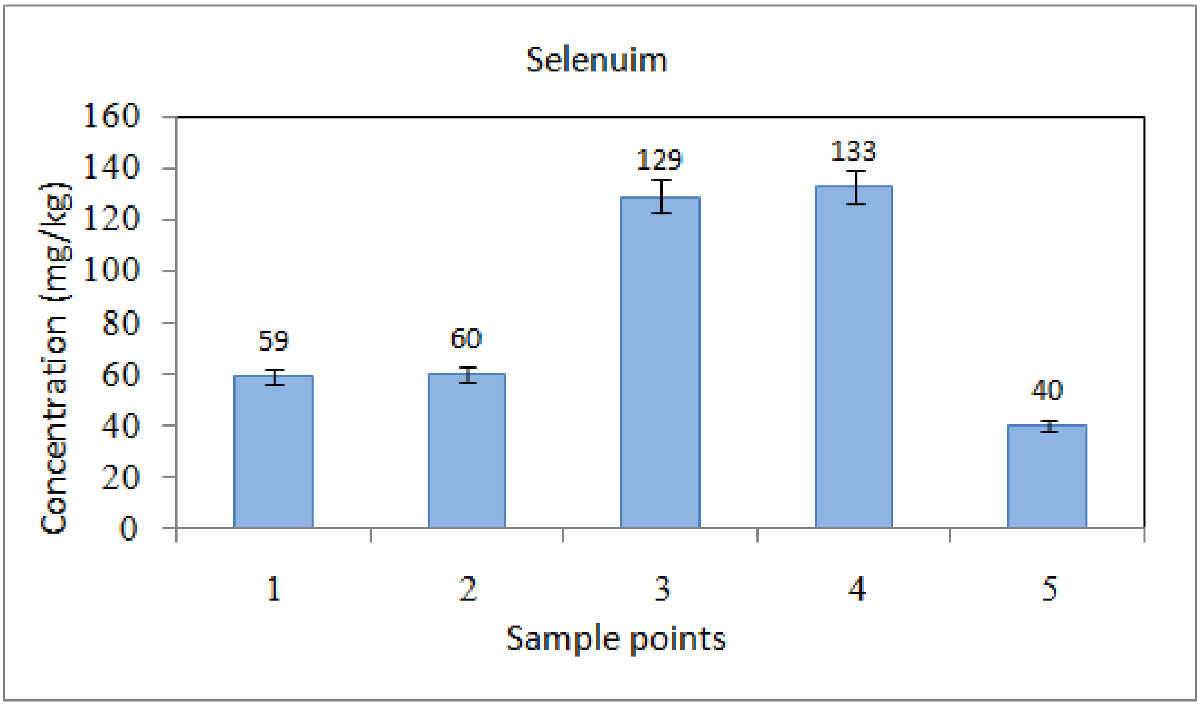

Figure 4f. Selenium concentrations in falling dust samples.

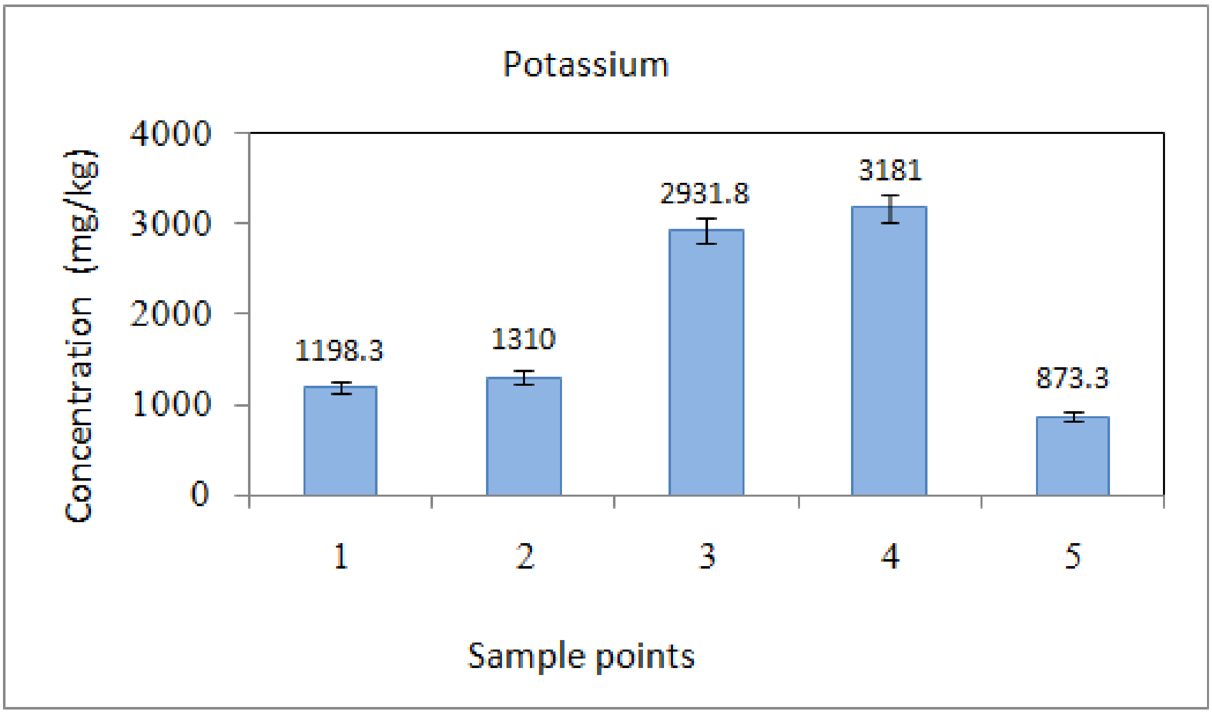

Figure 4g. Potassium concentrations in falling dust samples.

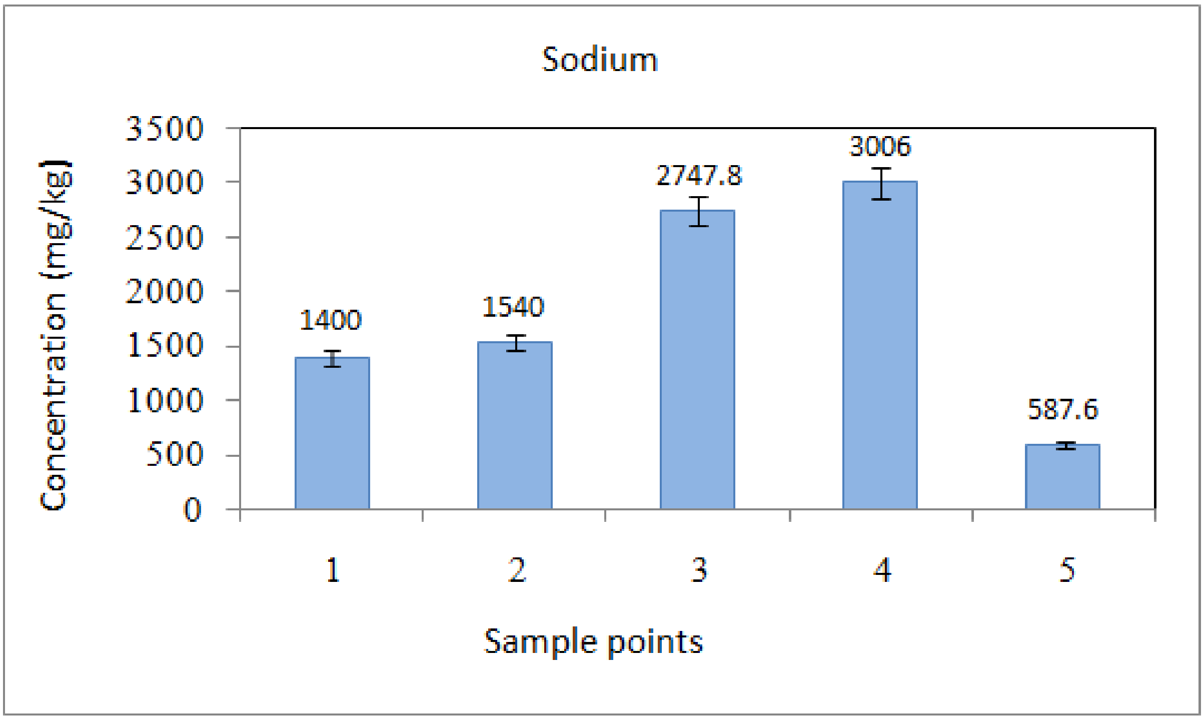

Figure 4h. Sodium concentrations in falling dust samples.

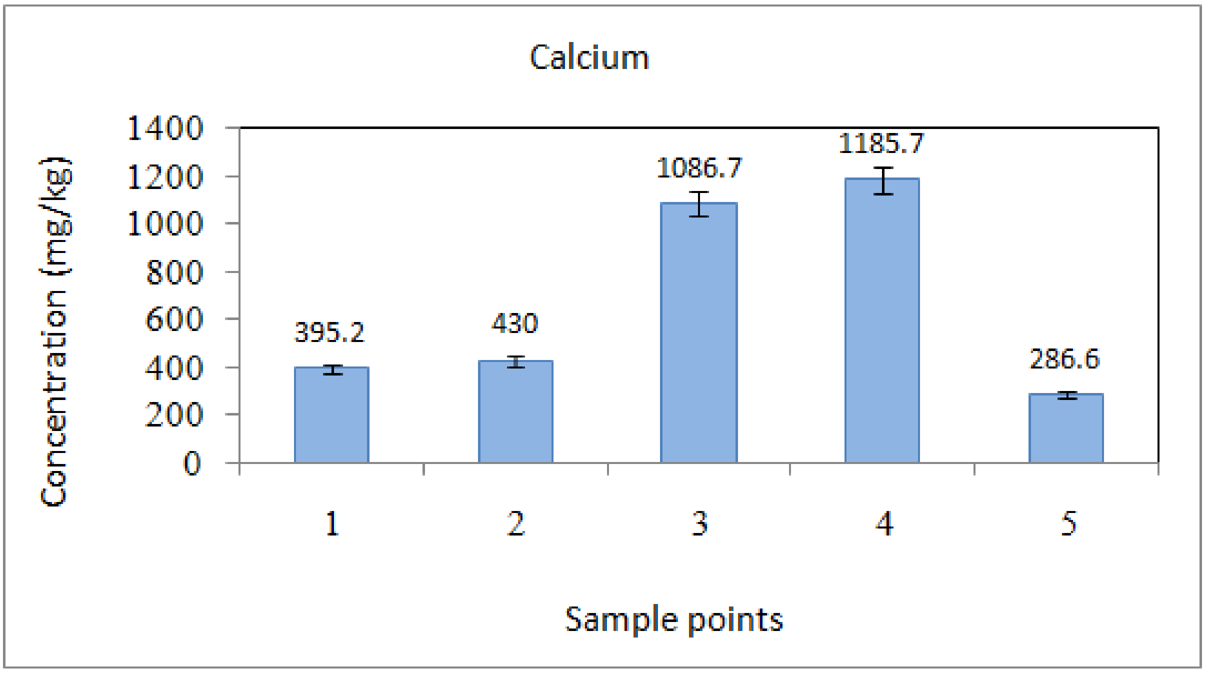

Figure 4i. Calcium concentrations in falling dust samples.

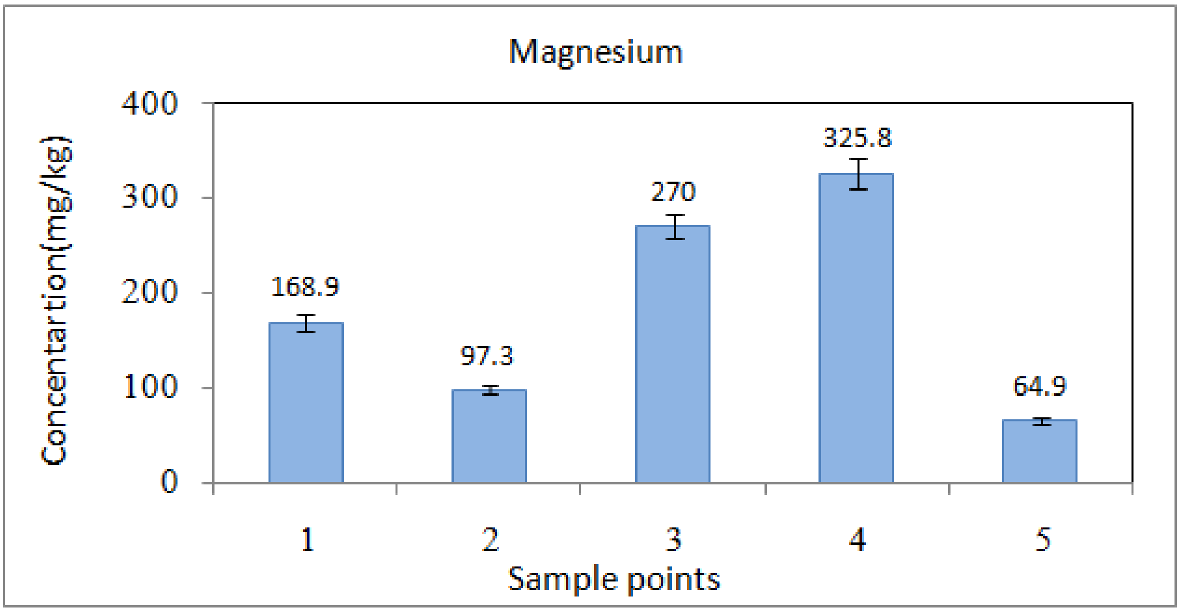

Figure 4j. Magnesium concentrations in falling dust samples.

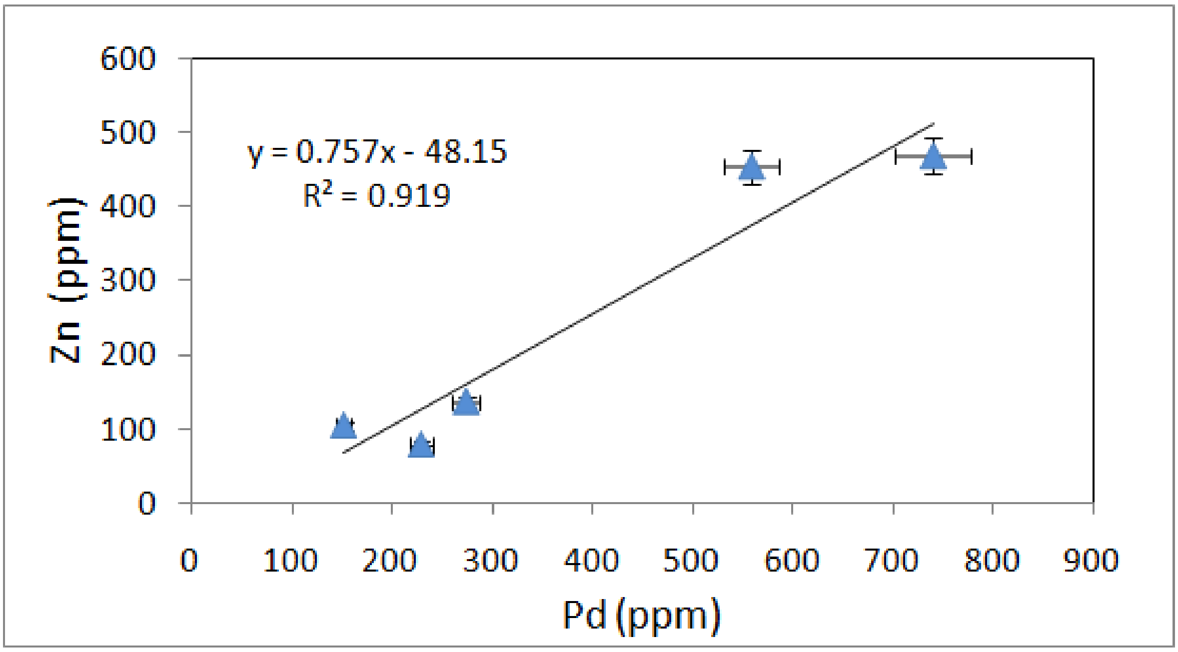

Figure 5a. Shown the correlation between Pb and Zn concentrations.

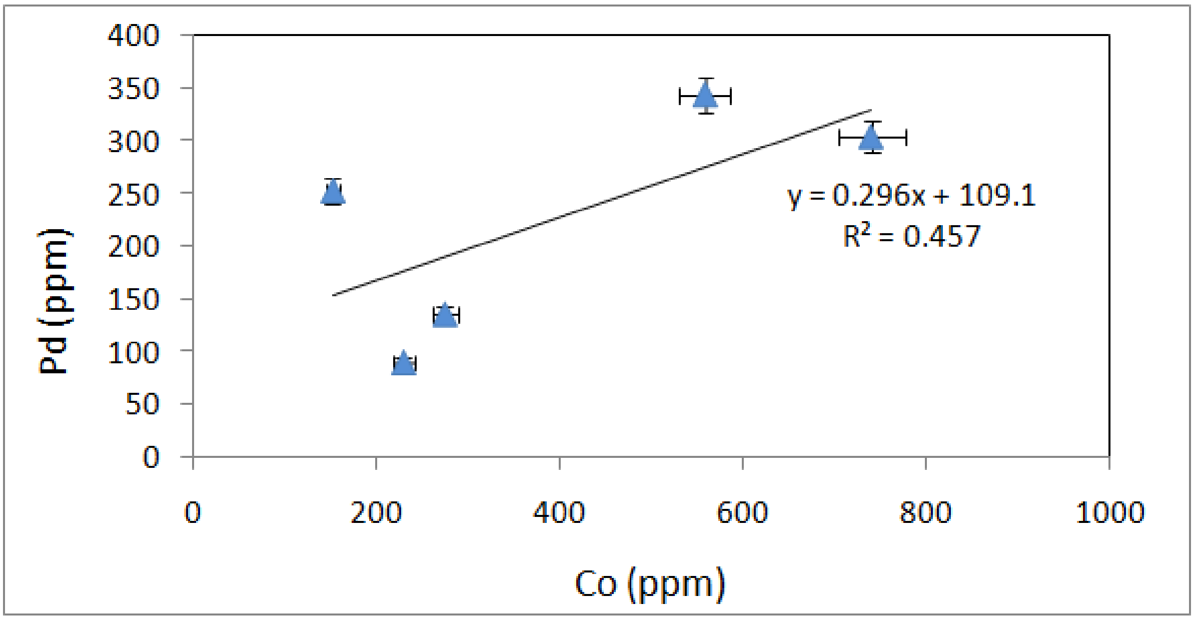

Figure 5b. Shown the correlation between Pb and Co concentrations.

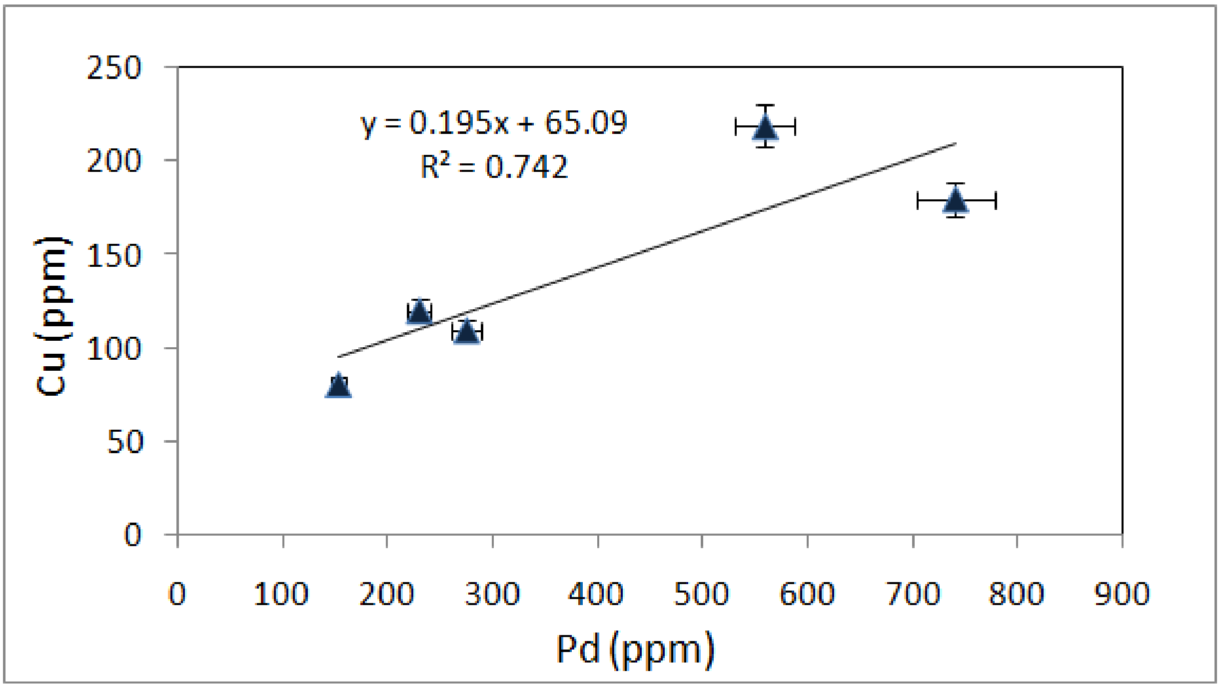

Figure 5c. Shown the correlation between Pb and Cu concentrations.

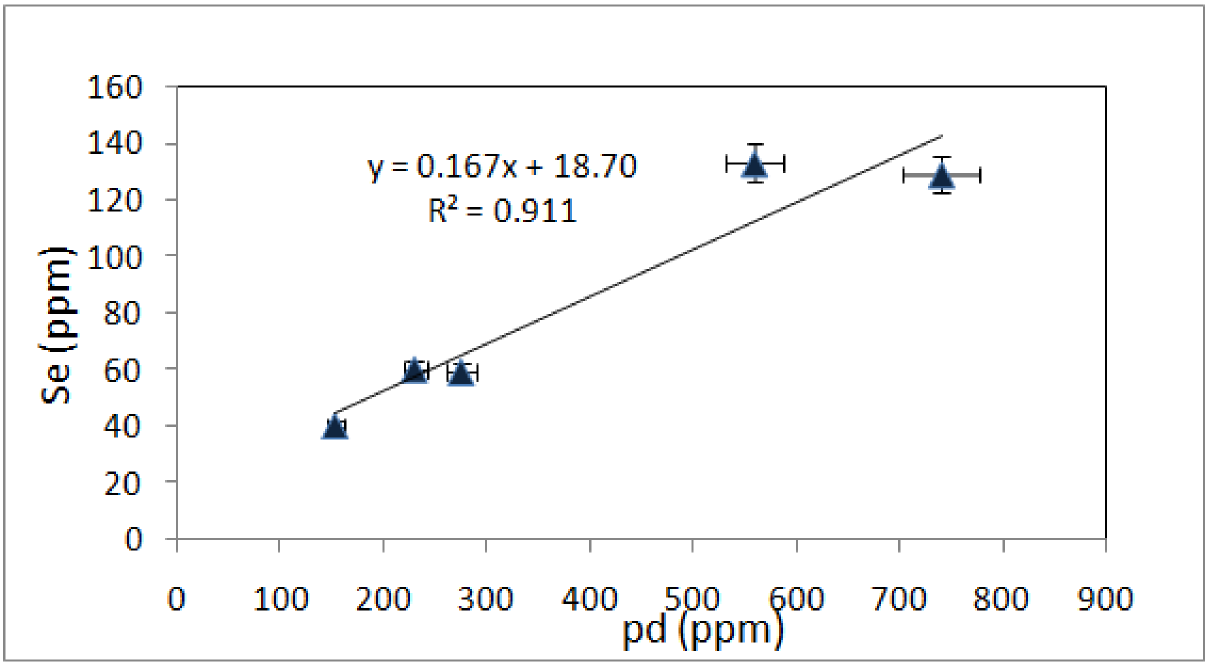

Figure 5d. Shown the correlation between Pb and Se concentrations.

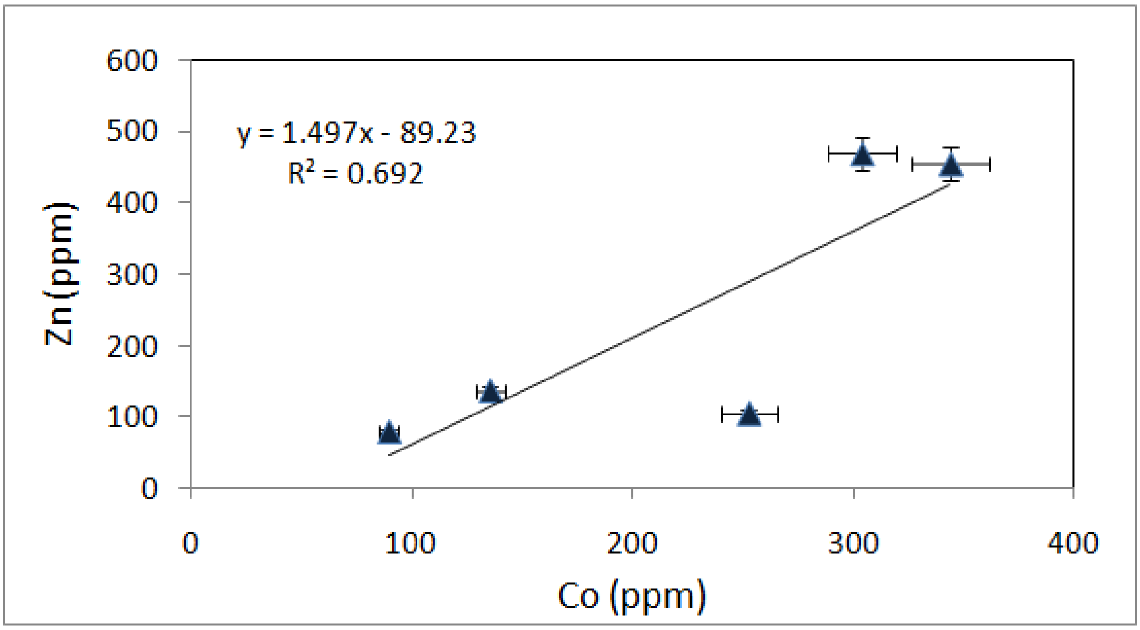

Figure 5e. Shown the correlation between Co and Zn concentrations.

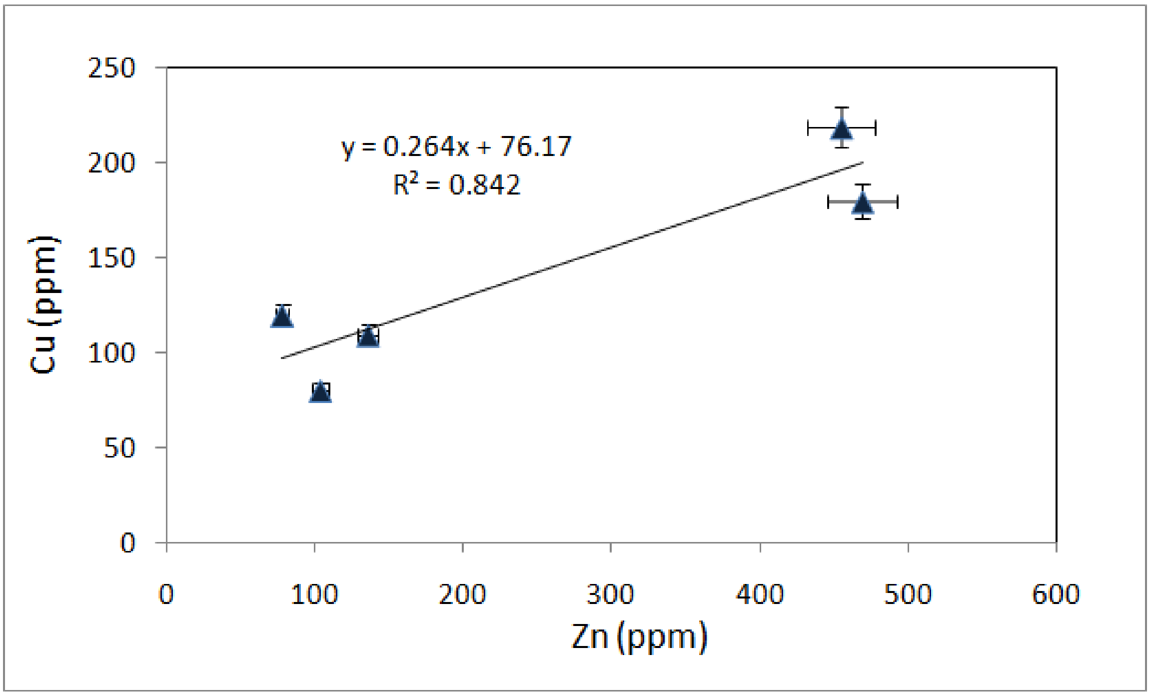

Figure 5f. Shown the correlation between Zn and Cu concentrations.

Conclusion

Aerosols metals pollutants and their impact on environmental and human health are one of the important concern over the world in recent years. In this study, the concentrations of aerosol falling dust were varied based on the location, but most of the aerosol metals were given higher concentrations than expected comparing with previous studies. In general, the concentrations of aerosols metals in this work were increased with increased the movement of traffic in that particular areas, density of population and industrial activities. This can be noticed in Garyuonis roadside and Tripoli roadside, which the highest concentrations for most measured elements. Aerosols metals concentrations may vary from place to place depending on pollutant types and accumulation and/or depositional factor. Specific metal abundance may indicate source and degree of contamination with respect to environmental stress. A significant positive correlation was observed between most pairs of studied aerosols metals. The concentrations of aerosols metals are given good profile for distribution of falling dust aerosols metals among Benghazi city, also revealed a better understanding of concentrations the levels of aerosols heavy metals contamination in studied areas.

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