Investigating the influence of emitted Cadmium from crude oil combustion on glutathione level in workers at Al- Qudis power plant, Baghdad

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Abstract

Al-Qudis power plant was chosen, as one of the power stations of Baghdad, to investigate the effects of Cadmium that emitted from combustion of crude oil in that power plant on the workers' glutathione serum level. Air samples were taken seasonally during August 2011- July 2012 from four sites at Al- Qudis power plant which are oil treatment unit 1(site 1), oil treatment 2 (site2), pre –chimney 1(site 3) and pre-chimney 2 (site 4), to measure levels of heavy metal (cadmium) under study**.** Blood samples were collected from the workers to estimate the heavy metal Cadmium. Air cadmium levels during summer (August and September) were varied from 6.26 ± 0.6 μg/m^3 at site 1 to 6.89 ± 0.67 μg/m^3 at site 3, while in spring (end of March, and end of April); these figures were ranged from 4.95 ± 0.39 μg/m^3 at site 4 to 6.08 ± 0.5 μg/m^3 at site 2. However, autumn (end of October and November) had mean values lied between 4.89 ± 0.6 μg/m^3 at site 3 and 5.7 ± 0.57 μg/m^3 at site 2. Winter (end of December 2011,January and February 2012)data gave a range of 4.51 ± 0.46 μg/m^3 at site 4 and 4.98 ± 0.57 μg/m^3 at site 3. The current results exceeded the acceptable levels of Cd for WHO which is around 0.3 μg/m^3. The results of current study showedthatthe mean value ofcadmiumin the blood of occupational sampleswas6.418 ± 0.636 μg/l which was significantly higher than those of ($P \leq 0.05$) environmental (5.247 ± 0.418 μg/l) and ($P \leq 0.01$) control (1.854±0.41 μg/l) samples.For reduced Glutathione (GSH) concentration, the current study results showed the highest value 5.4 ± 0.52 μmol/l in respect to control sample, while the lowest data 2.2595 ± 0.412 μmol/l and 2.6625 ± 0.475 μmol/l have been found in environmental and occupational samples, respectively.These results indicate that heavy metal (cadmium) influence GSH level of Al-Qudis's workers.

Keywords: Heavy metals, Power plant, cadmium, GSH.

التحري عن تأثير الكادميوم المنبعث من احتراق الوقود الخام في مستوى الكلوتاثيون للعاملين في محطة كهرباء القدس، بغداد

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الخلاصة

تم أختيار محطة كهرباء القدس أحدى محطات توليد الكهرباء في بغداد للتحري عن تاثير الكادميوم المنبعث من احتراق الوقود الخام في مستوى الكلوتاثيون المصلي للعاملين في المحطة. اخذت عينات الهواء

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موسميا من أب 2011 حتى تموز 2012 من اربعة مواقع في محطة كهرباء القدس وهي وحدة معالجة الوقود رقم 1 ووحدة معالجة الوقود 2 وموقع المداخن رقم 1 وموقع المداخن رقم 2 وذلك لقياس مستوى الكادميوم في الهواء،

وكذلك اخذت عينات دم العاملين في المحطة لتقدير تركيز الكادميوم في الدم. اظهرت النتائج ان معدل تركيز الكادميوم في الهواء خلال الصيف (شهري آب و أيلول) كان يتغير بين0.6 ± 6.26 مايكروغرام/م^3 في موقع رقم واحد و0.67 ± 6.89 مايكروغرام/م^{3}في موقع رقم 3 ، اما في الربيع (نهاية شهر آذار وشهر نيسان) فسجلت معدلات النتائج مدى من 0.39 ± 4.95مايكروغرام/م^{3}في موقع رقم 4 و ± 6.08 0.5مايكروغرام/م^{3}في موقع رقم رقم 2. في حين كانت معدلات نتائج الخريف (نهاية شهر تشرين الاول وتشرين الثاني سنة 2011)تتراوح بين 0.6 ± 4.89مايكروغرام/م^{3}في موقع رقم 3 و ± 5.7 0.57مايكروغرام/م^3. أما فصل الشتاء (نهاية شهر كانون الاول 2011 وشهر كانون الثاني وشهر شباط 2012) فقد سجلت النتائج مدى بين 0.46 ± 4.51مايكروغرام/م^{3}في موقع رقم 4 و ± 4.98 0.57مايكروغرام/م^{3}في موقع رقم 3. اظهرت النتائج الحالية حدا غير مسموح به حسب منظمة الصحة العالمية التي حددت تركيز الكادميوم في الهواء بحدود 0.3مايكروغرام/م^3. أظهرت نتائج الدراسة الحالية ان معدل تركيز الكادميوم في الدم للعينات المهنية كان 0.636 ± 6.418مايكروغرام/لتر وكان ذا فرق معنوي تحت مستوى 0.05 بالنسبة لتركيز الكادميوم في الدم للعينات البيئية حيث كان التركيز 0.418 ± 5.247 مايكروغرام/لتر ومعنوي جدا بالنسبة لتركيز الكادميوم في عينات السيطرة 1.854±0.41مايكروغرام/ لتر. بينت نتائج الدراسة الحالية انخفاضا في مستوى تركيز الكلوتاثيون المختزل بالنسبة للعينات البيئية والمهنية مقارنة مع عينات السيطرة حيث كانت التراكيز0.412 ± 2.2595 مايكرومول/لتر و ± 2.6625 0.475مايكرومول/لتر و 0.52 ± 5.4 مايكرومول/لتر، على التوالي. يمكن الاستنتاج من نتائج الدراسة ان هناك تأثير للكادميوم المنبعث من احتراق الوقود على مستوى الكلوتاثيون في دم العاملين في المحطة.

Introduction

Air pollution is a major environmental problem and it comes in a variety of forms, from visible particles of soot or smoke to invisible gases such as sulfur dioxide and carbon monoxide, and it can be created indoors and outdoors [1-3].There are many sources of air pollution like natural sources (volcanoes, fires and sea spray) and anthropogenic sources (municipal incinerators, personal generators emissions, highway vehicle, metal smelters and power plants emissions (fuel combustion)) [1]. Power plants emissions are a mixture of hundreds of constituents in either gas or particle form or semi-volatile matter [4, 5]. The generation of electric power plant is one important source of pollutants such as mercury, sulfur dioxide, nitrogen oxides and toxic heavy metals associated with fine particulate matter[6, 7].Although there is no clear definition of what a heavy metal is density is in most cases taken to be the defining factor. Heavy metals are thus commonly defined as those having a specific density of more than 5 g/cm^3[8, 9**].**

Most heavy metals are dangerous because they tend to bio-accumulate in the human body [8].The poisoning effects of heavy metals are due to their interference with the normal body biochemistry in the normal metabolic processes [9, 10].

The most toxic forms of these metals in their ionic species are the most stable oxidation states [9]. Most heavy metals produce reactive oxygen species, resulting in an increased lipid peroxidation (LPO), depletion of sulfhydryls, altered calcium homeostasis, and finally DNA damage [11, 12].

Beside major pollutants, fossil fuel combustion generates emissions of potentially toxic heavy metals [13]. Cadmium waslisted as one of the toxic heavy metals emitted from anthropogenic activities like power plant emissions [13-17].Cadmium is a heavy metal, which belongs to group 12B of the periodic table [18].It is an environmental contaminant that has been recognized as a risk factor in humans and animals [19, 20].Human beings are exposed to cadmium and cadmium compounds through occupational andenvironmental settings primarily via diet, drinking water and air, by slowly accumulating in the body[21].

Inhalation is the primary route of exposure in workplace where 5%-35% of inhaled cadmium is absorbed into the blood depending on its form, site of deposition, and particle size [22]. Non-occupational exposure to cadmium is cigarette smoke [20, 23].

Cadmium does not have any known useful biological functions and therefore not considered an essential metal [24, 25]. The natural sources of cadmium to the atmosphere are volcanic activity, forest fires and windblown transport of soil particles [25, 26]. During the 20^{th} century, cadmium emissions have increased dramatically because of an anthropogenic sources of cadmium to an environment which refining and use, copper and nickel smelting, phosphate fertilizers, which may contain high concentrations of cadmium and fuel combustion like diesel, petrol and coal [20, 27].

Cadmium has an extremely long biological half-life 30 years [28]. It has numerous undesirable effects on health in experimental animals and human, targeting the kidney, liver and vascular system in particular [29]. Upon chronic exposure in human, cadmium can cause irreversible renal tubular injury, osteoporosis, anemia, eosinophilia, anosmia, itai-itai, renal failure, atherosclerosis, high blood pressure and chronic rhinitis [30, 31].

Cadmium toxicity may be due to changes in enzyme activity, changes in proteins with sulfhydryl groups (thioneins), induction of oxidative stress and apoptosis, changes in the structure and/or function of cell membranes, inhibition of ATP production in mitochondria, and interaction with Zn, Cu, Ca, Se, and other essential metals [32, 33].

Glutathione is an important water-soluble antioxidant, synthesized from the amino acids glycine, glutamate, and cysteine [34]. It has an importance for cellular function.Reduced glutathione (GSH) is the most abundant thiol in cell which acts as an important antioxidant for cellular defense [35, 36].GSH is produced by the liver and is able to detoxify the lungs, RBCs, liver and the intestinal tract; it also removes a wide range of toxins, including those produced by heavy metals, cigarette smoke, alcohol, radiation and cancer chemotherapy [34]. The aim of this study was the interaction between cadmium and glutathione level in blood of Al-Qudis power plant workers.

Materials and Methods

Air sampling:

Al-Qudis power plant was chosen for this study, as one of the power stations of Baghdad, to investigate the effect of Cadmium that emitted from combustion of crude oil in that power plant. Al-Qudis power plant is located in north-east of Baghdad. Four sites were chosen as air sampling at the plant which is: Old oil treatment, new oil treatment and chimney unit 1, chimney unit 2. The samples were collected seasonally from August 2011 - July 2012 for measuring the levels of Cadmium. Units' emission particulate samples were collected for one hour, using rotary vane air sampling pump, which fixed on 1.5 m height level (breathing level); on cellulose ester membrane filters at an accurately known flow rate 16 L/min. The particles of units' emissions were precipitated on filters then Cadmiumconcentration wasestimated according to National Institute for Occupational Safety and Health (2003)[37].

Blood collection

Ten milliliters of peripheral blood samples were collected in plane tube from each of 90 male workers of the power plant's, which were divided into two groups, Oil treatment unit's workers which are occupationally exposed to exhaust and workers from other units which are environmentally exposed and from 20 persons not work at power station as control samples. The protocol of NOISH (1994) used to estimate blood Cadmium concentration of workers [38].

Standards and samples were analyzed by using flameless atomic absorption. Standard was also analyzed once every ten samples.

Glutathione (GSH) estimation:

GSHlevelestimatedAccording to Khan *et al.*[39]. 2.3 ml buffer was added to 0.2ml of the sample (serum) followedby addition of 0.5ml of DTNB.

The mixture wasthen analyzed by spectrophotometer. Blank consist of 2.5ml of buffer and0.5ml of DTNB was measured against a reference cellcontaining 3ml of buffer. All the measurements were carriedout at 412 nm after five minutes. UV/visible spectrophotometerof model 1601(Shimadzu) was used for absorbancereadings.

Results and Discussion

Cadmium in air:

Concerning air cadmium, the current results displayed that mean Cd air level in all sites during summer season were significantly higher than those of same sites but in remaining seasons followed by those of spring, autumn and winter seasons($P \leq 0.001$).

In summer season, the data of mean air Cd levels were varied from 6.26 ± 0.6 µg/m^3 at site 1 to 6.89 ± 0.67 µg/m^3 at site 3 figure-1. While, during spring, these figures were ranged from 4.95 ± 0.39 µg/m^3 at site 4 to 6.08 ± 0.5 µg/m^3 at site 2 figure-2. However, autumn had mean values lied between 4.89 ± 0.6 µg/m^3 at site 3 and 5.7 ± 0.57 µg/m^3 at site 2 figure-3.While, winter data gave a range of 4.51 ± 0.46 µg/m^3 at site 4 and 4.98 ± 0.57 µg/m^3 at site 3 figure-4.The current results exceeded the acceptable levels of Cd for WHO which is around 0.3 µg/m^3. In this regard, Barakat found TSP and heavy metals levels were high at summer season [40]. A study by Al- Khalidy found the levels of TSP in Al-Durah power plant were high during summer, while lead (Pb) concentration were high during winter [41], this attributed to kind of fuel used and the impurities within it, combustion process, efficiency of the production units, and also the place and directional setting of the instrumental air samplers. These factors agreed with the present study findings.

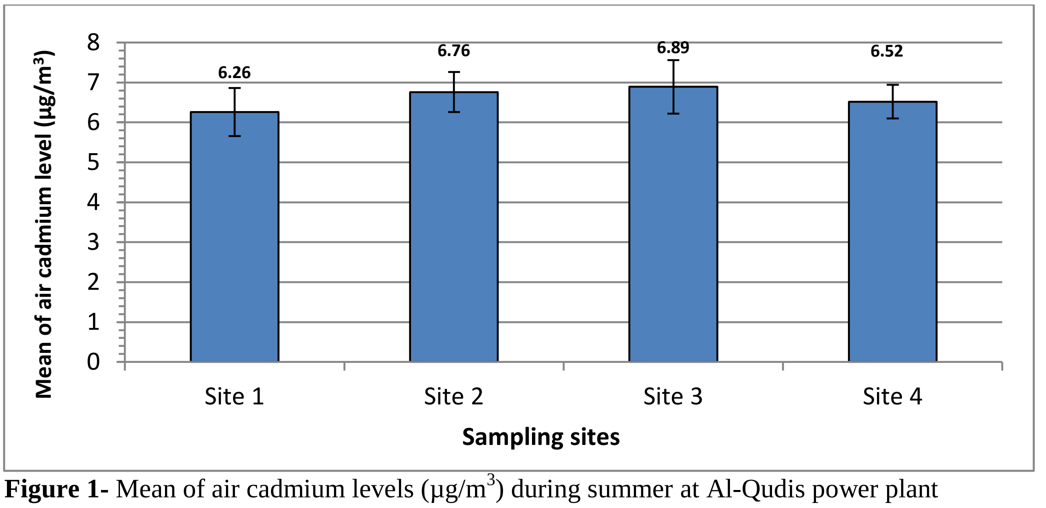

Figure 1- Mean of air cadmium levels (µg/m^3) during summer at Al-Qudis power plant

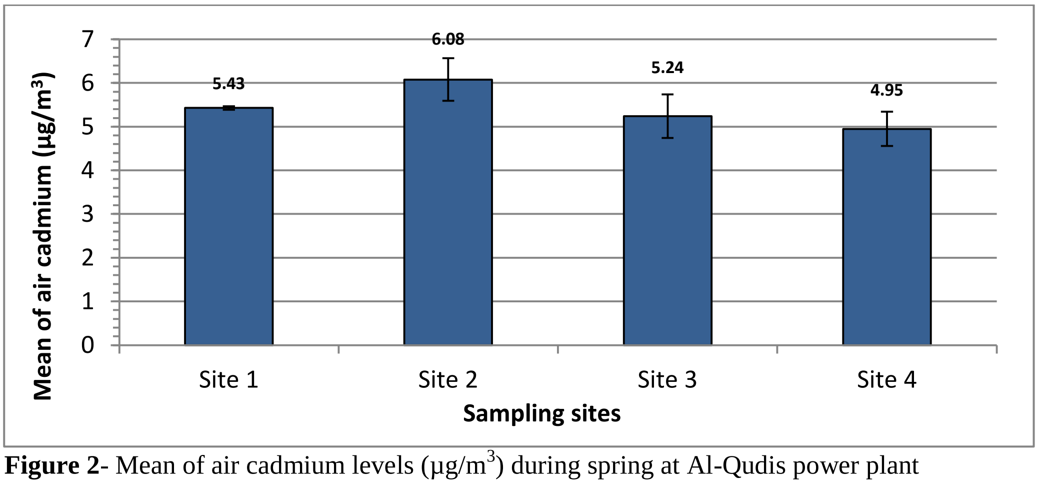

Figure 2- Mean of air cadmium levels (µg/m^3) during spring at Al-Qudis power plant

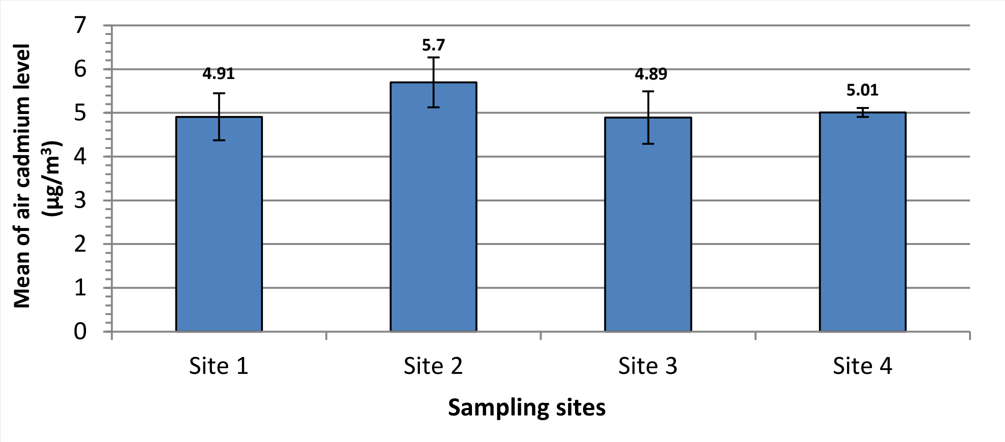

Figure 3- Mean of air cadmium levels (µg/m^3) during autumn at Al-Qudis power plant

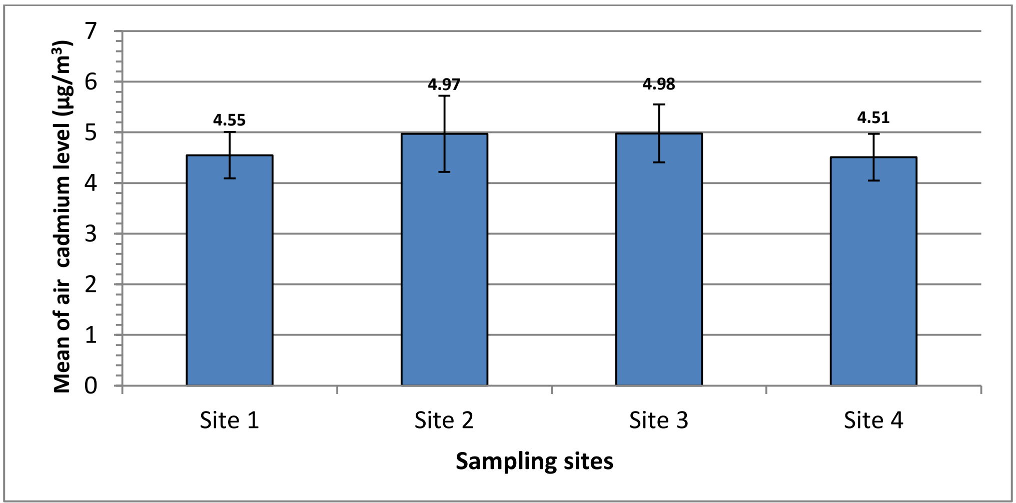

Figure 4- Mean of air cadmium levels (µg/m^3) during winter at Al-Qudis power plant

Cadmium in blood

Occupational sample of cadmium in blood content, had mean value of (6.418 ± 0.636 µg/l) which was significantly higher than those of (P≤ 0.05) environmental (5.247 ± 0.418 µg/l) and (P≤ 0.01) control (1.854±0.41 µg/l) samples figure-5.After inhalation exposure, some of the cadmium compounds are deposited in the airways or the lungs, and the rest is exhaled [19]. About 5-50% of the cadmium breathing will enter the body through the lung [23].The results also revealed insignificant effects regarding the exposure time period on the blood cadmium levels. This is returns to the fact that the cadmium was rapidly clears form the circulation system [23]; hence the level of Cd in blood shows resent exposure to Cd only [42]. On the other hand, the major portion of cadmium's burden in the body located in the liver and kidney [43,44].

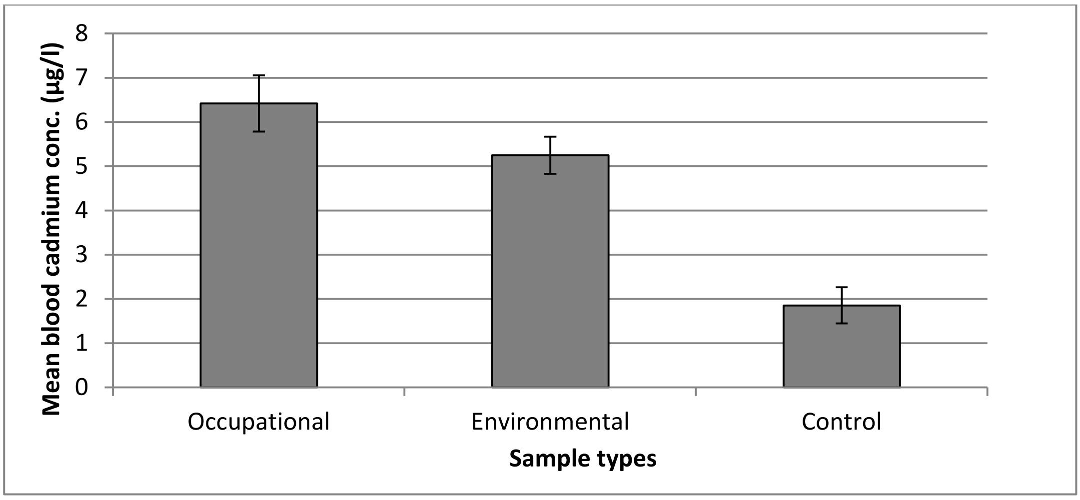

Figure 5- Mean blood cadmium concentration (µg/l) of workers at Al-Qudis power plant

Absorbed cadmium is excreted very slowly, with urinary and fecal excretion being approximately equal [45].

The highest mean level was appeared in occupationally exposed samples and this may be related to many reasons like processing the crude oil, lack of commitment with safety precautions.

Cigarette smoke is one of the non-occupational exposures to cadmium[20, 23]. This fact is given an explanation to the high levels of Cd in blood content of smokers. Zeneli*et al.* (2009)concluded that air pollution (from fossil fuel burning in power plant) and smoking were very important factors for the level of cadmium concentration in blood, which had an inhibitory effect in the syntheses of bilirubin [46].The presence of cadmium as a component of tobacco may be led to increasing levels of cadmium blood content [30]. Ibeto, *et al*. indicated that the high level of cadmium in blood of Nigerian people is due to impact of environmental pollution [47].

Occupational exposed to cadmium through the different industries that use cadmium and emission from combustion of fossil fuel led to high levels of blood cadmium [20, 27].

This increase in cadmium blood level could lead to many health problems like induction of oxidative stress and apoptosis, changes in the structure and/or function of cell membranes, changes in DNA structure and altered gene expression, inhibition of ATP production in mitochondria, and interaction with Zn, Cu, Ca, Se, and other essential metals [32, 33, 48]. Bizon*et al.*showed a positive relationship between the concentration of arsenic, lead and cadmium in the blood and urine of smelters, and smoking [49].

Glutathione (GSH) concentration

As shown in figure-6, the highest values (5.4 ± 0.52 µmol/l) of Glutathione concentration (GSH) was recorded for control sample, while the lowest values (2.2595 ± 0.412 µmol/l) and (2.6625 ± 0.475 µmol/l) have been found in environmental and occupational samples, respectively.However, current results show that control sample had significantly ($P \leq 0.001$) higher GSH concentration than those of both occupational and environmental samples due to LSD values which were 1.456 µmol/l and 1.372µmol/l respectively, but the differences between mean GSH of occupational and environmental samples were insignificant ($P > 0.05$) and the LSD value was 1.273µmol/l.This fact may be led to suppose that GSH concentration is effected by the air pollution (emissions of power plant). The reduction of GSH level was possibly due to its increased antioxidant activity and conjugation action with the xenobiotics present within fly ashes propelled by GST [50].

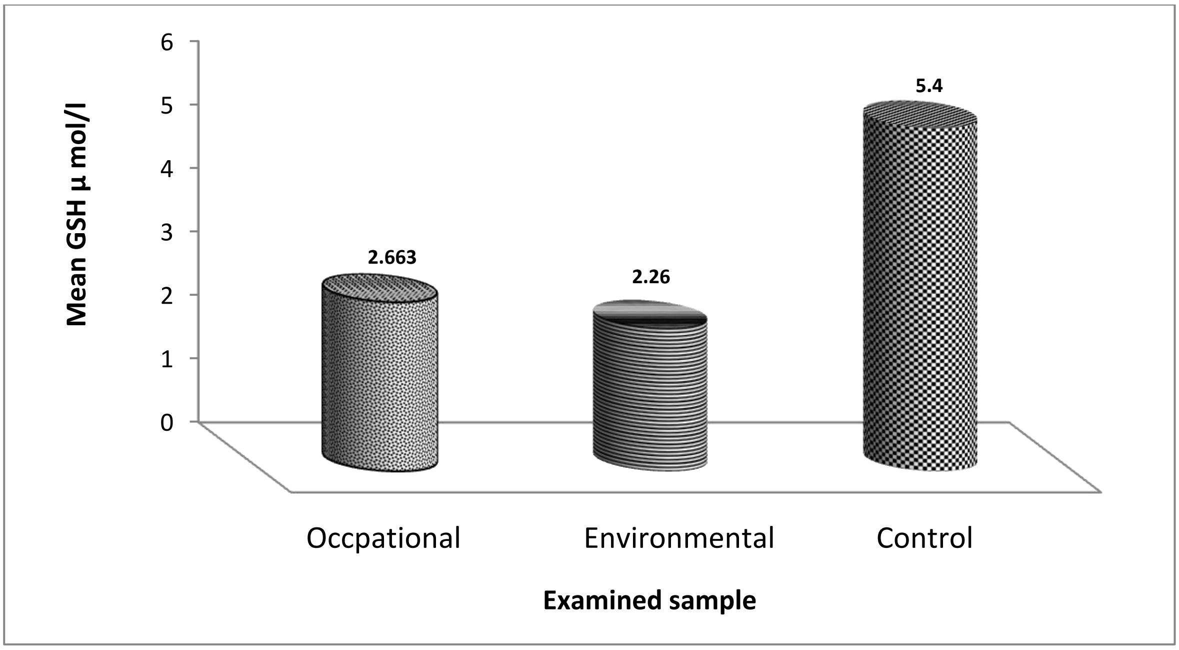

Figure 6- Mean of Glutathione (GSH) (µmol/l) concentration in occupational, environmental and control samples

A study by Khan *et al*.[39] found aluminum caused depletion of GSH concentration in plasma and attributed this to the interaction of reduced glutathione and aluminum either from oxidized Glutathione (GSSG) or Al-SG complex (heavy metals-SG complex).

Epidemiological studies had found that heavy metals, PAHs, and other particulate air pollution in urban environment could be associated with an increasing number of evidences demonstrated the involvement of reactive oxygen species (ROS) [51-53]. This oxygen species might lead to the formation of oxidative DNA damage [54]. According to Al-Helaly an increase exposure of different pollutants led to glutathione deficiency which contributes to oxidative stress in workers then decreased theantioxidant enzymes levels [55]. This behavior might give an indication for the oxidation that take place in exposed persons which plays a key role in aging and pathogenesis of many diseases, one of which is cancer [34, 50].Hall *et al.*[56]indicated that glutathione deficiency may be due to arsenic exposure.

Cadmium could induce cancer through the induction of oxidative stress [57]. From above results the present study concluded GSH reduction in occupational and environmental samples may be associated to the interaction of reduced GSH and heavy metal to form oxidized Glutathione (GSSG) or metals-SG complex, the TSP concentrations in the emissions of Al- Qudis power plant and smoking influence.

From above results the present study concluded GSH reduction in occupational and environmental samples may be associated to the interaction of reduced GSH and Cadmium to form oxidized Glutathione (GSSG) or metals-SG complex, the TSP concentrations in the emissions of Al- Qudis power plant.

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