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Concentration of heavy elements and metallothionein in the serum of workers in the industrial city of the Qar Governorat

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***Abstract*---**This study was conducted in biology department labs, college of science university of The-Qar in Iraq, designed during the period from October 2201 to May 2022. The purpose of the study is measuring the protein (metalothionine) and some heavy elements (Lead, Cadmium, Copper, Chromium and Selenium) in blood serum workers in the industrial city in Dhi-Qar Governorate, north of Nasiriyah city. The current study included 100 samples ranging in age from (21-55) years, 50 samples battery repair, and 50 samples of healthy people away from the industrial city and exposure direct pollutants as a control group. The results and statistical analysis showed illustrated the level of all elements increase significantly in battery repair group. Compared with control group. The results of the study also showed that concentrations of Cd, Pb, Cr, Cu and Se for battery repair workers were with a means (0.46 ± 0.12, 0.32 ± 0.06, 4.20 ± 0.82 , 1.98 ± 0.23, 0.33 ± 0.13) μg/dl respectively, and the concentrations of Cd, Pb, Cr, Cu and Se for healthy people were with a means (0.29 ± 0.01, 0.28 ± 0.04, 3.91 ± 0.71, 0.87 ± 0.14, 0.16 ± 0.03) μg/dl respectively. The results of the study also showed the concentrations of Metalothionin for battery repair workers were with a means (178.8 ± 35.5)pg/ml, for healthy people were (142.2 ± 25.0) pg/ml, showed illustrated the level of Metalothionin increase in battery repair group compared with control group. As a result of the high values of elements in this group due to the nature of their work and their direct contact with pollutants where the MTs play a key role in the metal metabolism.

***Keywords*---**Heavy elements, serum, Metalothionin, Human work place.

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1-Introduction

Occupational exposure the prolonged exposure to the various well-known environmental factors including heavy elements, air pollutants (particulate matter), nanoparticles containing metals, results in accelerating the progression some of diseases (Mir *et al.* 2020). Heavy elements exposure occurs significantly by occupational exposure, Workers of the mining and production of cadmium, chromium, lead, mercury, gold and silver have been reported to be thus exposed; also inhabitants around industrial sites of heavy elements mining and processing, are exposed through air by suspended particulate matters (Length, 2007) . Exposure to toxic heavy elements is generally classified as acute, 14 days or less, intermediate, 15-354 days, and chronic is more than 365 days, Because heavy elements are not easily biodegradable, it can accumulate in vital human organs, which cause varying degrees of sickness based on period and type of exposures (Demirezen and Aksoy, 2006).The acute toxicity is usually from a sudden or unexpected exposure to a high levels for short time of the heavy elements and a Chronic exposure may occur in either home or workplace, Symptoms of chronic toxicity are often similar to many common conditions and may not be readily recognized(Fatima Abbas, 2016). An accumulation of heavy elements in humans body can cause disruption of numerous biochemical processes, such as cardiovascular, nervous, kidney and bone diseases (Jarup, 2003) .

Heavy element are any metallic element that has a relatively high density and is toxic even at low concentration, they are a group of metalloids and element with specific density greater than 4 g/cm3 or 5 times greater than the water density, it occur as natural components of the earth crust and are persistent to environmental circumstance cannot be destroyed or degraded(Hussain, 2019) .It is the generic term for metallic elements having an atomic weight higher than 40.04 (the atomic mass of Ca) (Morais *et al.*, 2012).

Examples of common heavy element are chromium (Cr), lead (Pb), cadmium (Cd), mercury (Hg), copper (Cu) and zinc (Zn). Arsenic (As) is also included in this group because of similarities in physical and chemical properties, Less common heavy metals include iron (Fe), cobalt (Co) and manganese (Mn) (Kim et al., 2019). These element are quintessential to maintain various biochemical and physiological functions in living organisms when in very low concentrations, however they become noxious when they exceed certain threshold concentrations (Jaishankar *et al.,* 2014).

The exposure of humans to heavy element can occur through a variety of routes, which include inhalation as dust or fume, vaporization, and ingestion through food and drink. Prolonged exposure and higher accumulation of such heavy element can have deleterious health effects on human life, soil, air and aquatic biota(Singh *et al.,* 2018). Unlike organic contaminants element are not degradable and thus remain in the environment for long periods of time; when present at high concentrations (Kumar Ahirwar *et al.,* 2018).

Heavy element enter the surroundings by natural means and through human activities. Various sources of heavy element include soil erosion, natural weathering of the earth's crust, mining, industrial effluents, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others (Jaishankar *et al.,* 2014)

An excess amount of such element produces cellular and tissue damage leading to a variety of adverse effects and human diseases(Tchounwou *et al.,* 2012). Symptoms vary, depending on the nature and the quantity of the heavy element ingested. Patients may complain of nausea, vomiting, diarrhea, stomach pain, headache, sweating, and a metallic taste in the mouth. Depending on the metal, there may be blue-black lines in the gums(Roozbahani *et al.,* 2015)

In-depth studies in the past few decades have shown element like iron, copper, cadmium, mercury, nickel, lead and arsenic possess the ability to generate reactive radicals, resulting in cellular damage like depletion of enzyme activities, damage to lipid bilayer and DNA(Flora *et al.*, 2008)Various studies have investigated that carcinogenicity and mutagenicity of heavy element are associated with induction of oxidative stress. In this regard, researchers found that within the biological systems redox reactions are being performed by carcinogenic element ions such as chromium, nickel, vanadium, cobalt, and arsenic. Thus free radicals produced as a result of these reactions lead toward oxidative damage of proteins as well as DNA (Rehman *et al.*, 2018).

Metallothionein (MT) is a metal-binding protein with a low molecular weight and a high cysteine content found in all eukaryotes, The human MT gene is found on the q13 region of chromosome 16, MT can be roughly divided into four subfamilies in humans, designated as MT1, MT2 (also known as MT2A), MT3, and MT4(Dai *et al.,* 2021). Metallothionein (MT) is a family of cysteine-rich, low molecular weight (MW ranging from 500 to 14000 Da) proteins. They are localized to the membrane of the Golgi apparatus. MTs have the capacity to bind both physiological such as (zinc, copper, selenium) and xenobiotic (such as cadmium, mercury, silver, arsenic) heavy elements through the thiol group of its cysteine residues, which represent nearly 30% of its constituent amino acid residues (Sigel *et al.*,2009) .MT1 and MT2 are ubiquitously expressed in almost all organs, especially in the kidney, liver, intestine, and pancreas. MT3 is present in a variety of organs, including the brain, the heart, the retina, the kidneys, the breasts, the prostate, the bladder, and the reproductive organs, whereas MT4 is found predominantly in the stratified squamous epithelium (Wei *et al.*,2008). Their production is dependent on availability of the dietary minerals such as zinc, copper, and selenium, as well as the amino acids histidine and cysteine (Suhy *et al.*,1999). Metallothionein biosynthesis can also be induced by certain agents or conditions, for example, hormones, pharmaceuticals, alcohols, other substance treatments and many more(Wang *et al* 2014). MT1 is widely expressed in almost every organ to maintain homeostasis Under physiological conditions,MT1 is involved in regulating the steady-state of metal, alleviating heavy elements poisoning (Dai *et al.*, 2021).

Materials and Methods

The study groups were 50 Battery repair workers who were exposed to heavy elements and pollutants, the control group (50 individuals). After signing contract, a form including several questions such as age, weight, height, working time, duration of exposure, In addition, they were also asked about being smokers or non-smokers. this study recorded that all workers are male. The current study was conducted in the industrial cities in Thi-Qar Governorate, where the largest work group was found within the age group ranged from 21 to 50 years.

After approval, blood is drawn from the vein after sterilization of the place and withdrawn 6 ml of blood from male, to Serum Preparation a most 6 ml of blood was centrifuged (3000 rpm / min) for 20 minutes and divided into two parts evenly, then kept the serum at -20 ° C until. The digestion of serum was done based on (Ji and Ren, 2002) .

The measurement of heavy elements in the blood serum by Flame Atomic Absorption Spectrophotometer (FAAS.- Phoenix 986 AA. United kingdom-UK.) was done based on procedure of manufacturer. The measurement of Metallothionein in the blood serum has been done by ELISA device. The statistical analysis is performed with Excel application (version 2010) for Windows 7 and Statistical Package for the Social Sciences (SPSS) (version 22) . T-test used for independent, P-value ≤ 0.05 was considered statistically significant .

Results and Discussion

The current study illustrated that the level of all elements increase significantly in battery repair group compared with control group, as showed in table (1) because these elements are an essential material in the manufacture of most types of batteries, as the human body does not know how to eliminate the toxic metals present in the battery, which leads to their permanent accumulation and reaching concentrations that are considered harmful to most of the organs of the human body , in study a study by Lormphongs *et al.,* (2003) , in Thailand was conducted in a battery manufacturing plant where lead was used in the processes of production, where high levels of lead in the blood ,and in study conducted by Qammar (2021) on a group of workers oil field workers in Al-Nassiriyia city south of Iraq assessment to aryl hydrocarbon receptor , Cytochrome p450 and heavy metals , increase in the level of cadmium in the blood of workers compared to the control group ,this agrees with a the current study , the current study inconsistent with the study mentioned by Alli, (2015) to measure blood cadmium level of occupationally exposed individuals in Nigeria .

Table 1. Assessment of heavy elements in serum of the studied groups

Parameters Groups	Cases No.	Mean ± SD mg/dl				
		Cd	Pb	Cr	Cu	Si
Battery R	50	0.46 ± 0.12	0.32 ± 0.06	4.20 ± 0.82	1.98 ± 0.23	0.33 ± 0.13
Control	50	0.29 ± 0.01	0.28 ± 0.04	3.91 ± 0.71	0.87 ± 0.14	0.16 ± 0.03
P. value		< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

According to Smoking in both smoking and non-smoking groups the results investigated a significant increase of Cd, Cu and Se concentration in battery repair group, compared with control group, as showed in table (2). The Cd and Pb are absorbed by the body through the lungs and the digestive tract, in the work environment, route of absorption plays an important role in the case of bad hygienic habits such as not washing contaminated hands, ingestion of contaminated food or smoking during occupational exposure (Marigómez, 2014) . This study is consistent with a previous study by .Milde *et al*., (2004) on patients with colon cancer ,The study was recorded high values of Cu in blood serum of smoker workers.

Table 2. Assessment of heavy elements in studied groups and control according to smoking

Heavy elements	Cases No	Battery Repair		Cases No	Control group		p. value
		Non-Smoker	Smoker		Non-Smoker	Smoker	
Cd mg/dl	18:32	0.47 ± 0.010	0.046 ± 0.013	26:24	0.31 ± 0.011	0.027 ± 0.007	< 0.01
Pb mg/dl	18:32	0.30 ± 0.03	0.33 ± 0.07	26:24	0.28 ± 0.05	0.29 ± 0.04	< 0.01
Cr mg/dl	18:32	4.40 ± 0.88	4.09 ± 0.78	26:24	4.00 ± 0.74	3.82 ± 0.66	< 0.01
Cu mg/dl	18:32	2.05 ± 0.31	1.95 ± 0.17	26:24	0.92 ± 0.14	0.81 ± 0.12	< 0.01
Se mg/dl	18:32	0.32 ± 0.10	0.33 ± 0.12	26:24	0.15 ± 0.04	0.17 ± 0.03	< 0.01

According to the age groups in battery repair group showed a significant increase in second age group compared with first age group as showed in table (3) , because heavy elements are not biodegradable, they are stored over time in various body tissues such as bones, liver, spleen, kidneys, hair, nails, teeth, and the central nervous system ,and the results showed a significant increase of concentration Pb , the Pb is metal which have long half time in men from 10 to 30 years. This explain the rising of Pb with age in collected sample of present study.

Table 3.A. Assessment of Cd concentration in serum of the studied group and control according to age group

Cd Age Groups	Mean ± SD	
	Battery R	Control
21 – 30 years	0.47 ± 0.008	0.25 ± 0.010
31 – 40 years	0.52 ± 0.013	0.29 ± 0.005
Above 40 y	0.40 ±0.011	0.33 ± 0.012
P. value	0.008	0.096

Table 3.B. Assessment of Pb concentration (mg/dl) in studied groups and control according to age groups

Pb Age Groups	Mean ± SD	
	Battery R	Control
21 – 30 years	0.35 ± 0.06	0.28 ± 0.06
31 – 40 years	0.29 ± 0.09	0.28 ± 0.04
Above 40 y	0.31 ± 0.01	0.29 ± 0.04
P. value	0.05	0.934

Table 3.C. Assessment of Cr concentration (mg/dl) the serum of the in groups and control according to age groups

Cr Age Groups	Mean ± SD	
	Battery R	Control
21 – 30 years	4.08 ± 0.82	3.75 ± 0.44
31 – 40 years	4.35 ± 0.81	3.87 ± 0.70
Above 40 y	4.17 ± 0.87	4.08 ± 0.86
P. value	0.651	0.934

Table 3.D. Assessment of Cu concentration (mg/dl) in the serum of the groups and control according to age groups

Cu Age Groups	Mean ± SD	
	Battery R	Control
21 – 30 years	1.92 ± 0.14	0.917 ± 0.15
31 – 40 years	2.06 ± 0.33	0.85 ± 0.13
Above 40 y	1.94 ± 0.18	0.85 ± 0.15
P. value	0.256	0.421

Table 3.E. Assessment of Se concentration in (mg/dl) in the serum of the in studied group and control according to age groups

Se Age Groups	Mean ± SD	
	Battery R	Control
21 – 30 years	0.27 ± 0.06	0.16 ± 0.03
31 – 40 years	0.40 ± 0.16	0.18 ± 0.03
Above 40 y	0.30 ± 0.11	0.14 ± 0.04
P. value	0.007	0.002

The current study illustrated the level of metalothionin increase significantly in battery repair group compared with other groups, as a result of the high values of elements in this group due to the nature of their work and their direct contact with pollutants where the MTs play a key role in the metal metabolism.

Table 4. Assessment of Metalothionin (pg/ml) in serum of the studied groups

Metalothionin Groups	Cases No.	Mean ± SD(pg/ml)
Battery R	50	178.8 ± 35.5
Control	50	142.2 ± 25.0
P. value		< 0.001

According to Smoking in both smoking and non-smoking groups the results showed a significant increase of metalothionin concentration in battery repair group compared with groups , the MTs play a key role in inflammatory diseases where modulates immune responses to control inflammatory diseases.

Table 5. Assessment of Metalothionin in studied groups and control according to smoking

Metalothionin Groups	Cases No.	Mean ± SD	
		Non-Smoker	Smoker
Battery R	18:32	171.8 ± 30.7	182.8 ± 37.8
Control	26:24	141.0 ± 27.0	143.5 ± 23.1
P. value		< 0.01	< 0.01

According Age Groups In both studied groups and control group the results showed a non-significant differences in concentration of metalothionin.

Table 6. Assessment of metalothionin in serum of the studied group and control according to age groups

Metalothionin Age Groups	Mean ± SD (pg/ml)	
	Battery R	Control
21 – 30 years	167.3 ± 35.3	138.3 ± 23.9
31 – 40 years	187.5 ± 37.2	140.0 ± 24.4
Above 40 y	180.1 ± 33.1	147.4 ± 26.8
P. value	0.276	0.546

Conclusions

1) High concentrations of heavy elements in blood serum of workers at industrial city were more than in blood serum of the control group.
2) The obtained results show that smoking does not have a big impact on the concentration of heavy elements may be due to the individual differences of the physiological or physical.
3) Increase of Cd Concentration significantly in serum of battery repair group.
4) No clear effect is observed for age group on heavy elements and metalothionin in the workers blood serum.

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