

**Evaluation the Levels of Lead and Cadmium in Three Libyan Hospitals
Wastewater and Compare With the Levels of Lead and Cadmium in
Industrial and Domestic Wastewater in Three Libyan Cities**

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الملخص

أجريت هذه الدراسة لتقييم مستوى عنصر الرصاص وعنصر الكاديوم في المستشفيات العامة الليبية في ثلاثة مدن غرب طرابلس (مستشفى الزاوية المركزي ومستشفى صبراتة التعليمي ومستشفى صرمان العام) ومقارنة النتائج بمستوى الرصاص والكاديوم في مياه الصرف الصحي المنزلي ومياه الصرف الصحي الصناعي في نفس المدن لتحديد المصدر الرئيسي لتلوث مياه الصرف الصحي بواسطة بعض العناصر الثقيلة مثل الرصاص والكاديوم .

أخذت ثلاث عينات من كل موقع من مياه الصرف الصحي لثلاث مستشفيات من المدن الثلاثة الزاوية و صبراتة و صرمان) وأيضاً جمعت ست عينات من حجرة التفتيش العامة (مياه الصرف الصحي المنزلي , مياه الصرف الصحي الصناعي) من مواقع مختلفة لكل مدينة حيث استعملت كمجموعة مقارنة. وتم إجراء التحاليل والقياسات اللازمة لكل عينة بمعامل قسم علم البيئة بمصفاة تكرير النفط بالزاوية بواسطة (جهاز قياس الطيف الذري) . ولقد لوحظ إن منطقة الزاوية سجلت أعلى مستوى لكل من عنصري الرصاص والكاديوم في كلا من الجزء السائل والجزء الصلب يليها منطقة صبراتة ثم منطقة صرمان على التوالي وسجلت أعلى نسبة في مياه الصرف الصناعي لكلا المعدنين (الرصاص – الكاديوم) يليه مياه الصرف الصحي بالمستشفيات ثم مياه الصرف الصحي المنزلي . وأوضحت دراستنا انه لا بد من زيادة الوعي واتخاذ الحيطة اللازمة وإتباع الطرق السليمة للتخلص من مياه الصرف الصحي وذلك بإتباع إستراتيجية مجربة واثبت نجاحها لعلاج وتصريف مياه الصرف الصحي .

Abstract

This study was done to evaluate the level of Lead and Cadmium in Libyan general hospital's wastewater in three cities western of Tripoli (El-Zawia central hospital Subrata teaching hospital and Surman General hospital) and compare the obtained results with the level, of Lead and Cadmium in domestic and industrial wastewater of the same cities, to determine which the major source of pollution of wastewater in three cities by heavy metals such as Lead and Cadmium.

Three samples were taken from wastewater of three hospitals from each city. Another Six samples from each city were collected from general sewer system (Domestic and Industrial wastewater) from the cities from different locations which used as comparison group. The content of heavy metals (cadmium and lead) in wastewater and sludge were determined in Environment Laboratories Department with El-Zawia Petroleum Refinery by atomic spectrometric method.

Both lead and cadmium concentrations ($\mu\text{g/L}$) were significantly elevated in waste water; either solid or liquid waste water in all examined regions (El-Zawia, Subrata and Surman), Generally, El-Zawia region had the highest values of solid and water waste for both lead and cadmium levels followed by Subrata and Surman regions, respectively. We also found that both lead and cadmium residues were significantly high in industrial waste water then hospital then home either solid or liquid wastes. From this study, it can be said that there is an urgent need to raising awareness and education on wastewater issues. Proper wastewater management strategy is needed to ensure health and environmental safety.

Introduction

Wastewater is referred to any water, whose quality has been adversely being abused by anthropogenic influence. This includes liquid waste discharged from domestic home, industries, agricultural and commercial sectors. (Ekhaise and Omavwoya, 2008)

Nowadays in many societies, access to healthy water and the amount of water consumption are considered as aspects of sanitation situation and development of societies. The consumed water in daily life is recycled to primary source in some ways, but it is in the form of a liquid containing the consumed water and different contaminants that are entered during consumption. One of the important environmental problems which are increased by population growth is the spread of wastewater contaminants, for example hospital wastewater which results in surface and underground water contaminations. Specifications of hospital wastewaters, have made these kind of wastewaters special in environmental contaminations control issue (Jolibois and Guerbet, 2005)

Hospital wastewater has similar quality to municipal wastewater and important sources of pharmaceuticals residues in all wastewater treatment plant (WWTP) effluents due to their inefficient removal in the conventional systems, Moreover, Hospital wastewater includes a great variety of micro-contaminants that are chemicals, heavy metals, disinfectants and specific detergents resulting from diagnosis, laboratory, research activities and medicine excretion by patients. Indeed hospital wastewater may have an adverse impact on environmental and human health; therefore, the proper management of hospital wastewater quality and quantity is needed (Hanan and Amira, 2011).

All metals are toxic and our bodies require special transport and handling mechanisms to keep them from harming us. The toxicity occurs in humans due to environmental pollution via soil or water contamination or due to occupational exposure. Some of these metals are useful to us in low concentrations but are highly toxic in higher concentrations. These metal toxicity cause serious morbidity and mortality. (Suranjana and Manas, 2009).

Toxic metals are often discharged by a number of industrial processes and this can lead in turn to the contamination of freshwater and marine environment. The release of industrial wastewater containing cadmium to the environment is strictly controlled due to the toxic nature of soluble cadmium cations. Heavy metals are major pollutants in marine, ground, industrial and even treated wastewaters. Industrial waste constitutes the major source of various kinds of metal pollution in natural water. (Gravris *et al.*, 2010)

Cadmium is found in batteries, cigarette smoke, incineration of tyres, rubber, plastic, vending machine soft drinks. Cadmium toxicity causes liver, kidney damage, prostate dysfunction, bone diseases and cancer. Mercury enters body from dental amalgams, felt, laxatives, tattooing etc. and can cause adrenal dysfunction, damage to the central nervous system, hypothyroidism and nerve fiber degeneration. Nickel is present in hydrogenated fats and oils, stainless cookware, tea, tobacco smoke. Nickel toxicity causes kidney dysfunction, disruption of hormone and lipid metabolism and intestinal cancer. Lead is present in auto exhaust, hair dyes, in paints, in sindoor (vermillion), in surma (collyrium), glazing of pottery and enamel ware. Lead toxicity causes co-ordination and concentration lost, decreases Intelligence Quotient (I.Q), causes infertility, memory loss, especially long term memory, causes mood

swing and sterility. Heavy metal overload in the environment causes growth of stealth pathogens and also combinations of certain metals increases toxicity while other combinations reduces it e.g., lead makes mercury 100 times more toxic, (Suranjana and Manas, 2009).

Objectives of the study

The objectives of this study are:

To evaluate the level of Lead and Cadmium in general hospital's, domestic and industrial wastewater in three cities western of Tripoli (El- Zawia central hospital, Subrata teaching hospital, and Surman general hospital) in Libya

To compare the levels of Lead and Cadmium in different previous sources and regions.

Also determine which the major source of wastewater pollution in three cities by heavy metals such as Lead and Cadmium.

Literature review

Wastewater is defined as water that results from domestic use and could be mixed with industrial wastewater of a quality which meets the connection requirements set by the official body (AL-Shreideh, 2001). Urban wastewater is a combination of domestic effluent consisting of black water (extra, urine, and associated sludge), grey water (kitchen and bathroom wastewater) and water from commercial establishment and institutions, including hospitals, industrial effluent storm water and other urban (Hamdy and Regab, 2005).

Wastewater generally divided into two broad classifications: domestic wastewater and industrial wastewater. Domestic wastewater comes from communities of homes, businesses, and institutions. Domestic wastewater is 99.9% water and only 0.1% solids. The solids in domestic wastewater are both dissolved and suspended solids.

Wastewater is not just sewage. All the water used in the home that goes down the drains or into the sewage collection systems is wastewater. This includes water from baths, showers, sinks, dishwashers, washing machines, and toilets.

Municipal wastewater is mainly comprised of water (99.9%) together with relatively small concentrations of suspended and dissolved organic and inorganic solids. Among the organic substances present in sewage are carbohydrates, fats, soaps, synthetic detergents, proteins and their decomposition products, as well as various natural and synthetic organic chemicals from the process industries connected to the sewer systems.

The solids in wastewater can be attributed to various domestic and industrial activities it is estimated that the typical per person contribution of solids to domestic wastewater is 250 grams per day. The majority of this total is from wash waters (sinks, baths, laundry, etc.). The typical fecal amount is approximately one fourth of the total per person solids contribution. The use of home water softeners in areas with hard water (Metcalf and Eddy, 1991)

Municipal wastewater also contains a variety of inorganic substances from domestic, hospitals and industrial sources, including a number of potentially toxic elements such as arsenic, cadmium, chromium, copper, lead, mercury, zinc,...etc (Kenneth and Kerri, 1998).

The hospital wastes are produced mainly by public and private hospital an infrastructures (Tahiri et al., 2012). Hospitals represent an incontestable release source of many chemical compounds in the environment due to laboratory activity or medicine excretion into wastewater (Kummerer, 2001).

Generally, the hospital waste is classified into seven components, which comprises of both liquid and dissolved substance generated within the hospital environment (Heen, 1999 and FEPA, 1991). The most non hazardous infectious wastes which include kitchen waste, paper and plastics, hazardous components include, parts of human, blood, fetus and body fluid, infectious wastes, this include culture and stock of infective agents from laboratory waste, waste from surgery, etc, pharmaceutical wastes, all of this may found as a hospital wastewater contaminants (Agarwal, 1998).

Hospitals represent an incontestable release source of many chemicals compounds in the aquatic environment due to laboratory activity or medicine excretion into wastewater (Kummerer and Helmers, 2001).

The dosage of pollutants of hospital origin shows that certain substances, such as Anti-tumor agents, Antibiotics and Organ halogen compounds, leave mostly wastewater treatment plants (Chitnis *et al.*, 2004). By leaving the wastewater treatment plants, these chemical compounds can provoke the pollution of the natural environment by entailing a biological imbalance. In case the environmental conditions allowing the degradation of these substances are not gathered, they can exercise negative effects on the receiving waters and the living species (Chitnis *et al.*, 2000).

The hospitals wastewaters in comparison with domestic wastewaters which include microorganisms, detergents, oil and grease, nitrogen, phosphor, organic and mineral material, contain microorganism, dangerous radioactive materials, detergents and etc. In the hospitals which used these materials, it should be consider that the conservation of public health and insurance the sanity in the society is one of the most important aim of collecting and treating of the wastewater that for treating this amount of substances, there is a necessary need at the hospital for wastewater treatment plant. If this kind of wastewater was not well treated and buried, it will be the source of pollution distribution (Salvato, 1992).

Industrial wastewater is one of the important pollution of the water environment. During the last century a huge amount of industrial wastewater was discharged into river, lakes, and coastal areas. This resulted in serious pollution problems in the water environment and caused negative effects to the ecosystem and humans life. There are many

types of industrial wastewater based on different industries and contamination; each sector produces its own particular combination of pollutants. Like the various characteristics of industrial wastewater.

The amount of wastewater depends on the technical level of process in each industry sector and will be gradually reduced with the improvement of industrial technologies. the increasing rates of industrial wastewater in developing countries are thought to be much higher than those in developed countries. This fact predicts that industrial wastewater pollution as a mean environment pollution problem, will move from developed countries in the early 21st century (Hanchang, 1994).

Increasing heavy metals pollution which are harmful for the growth of the living organisms has been the subject of considerable interest (Wang *et al.*, 2008). The development of the industry and expansion of the chemical compounds used in different branches of industry are leading to the environmental spread of heavy metals (Tiller, 1989). For many people, heavy metal pollution is a problem associated with areas of intensive industry. However, roadways and automobiles now are considered to be one of the largest sources of heavy metals (Omgbu and Kokogbo, 1993).

One of the major causes of environmental pollution is the use of sewage sludge in agriculture (Nouri, 1980 and Nouri *et al.*, 2008).

Sewage sludge is the residue from the treatment of domestic and industrial wastewater. It contains useful organic matter and nutrients for plants. High cost of inorganic fertilizers and high inflation rates in most developing countries have resulted in waste materials like sewage sludge providing an alternative cheap input of nutrients in agriculture (Cooke,

1982). Sewage sludge does not only provide a cheap source of fertilizer, but it also solves the problem of waste disposal and protects the resource base and their reuse.

The continual use of sewage sludge can result in accumulation of heavy metals and other toxic materials in soil and crops in particular leafy vegetables (Abdel-Ghani *et al.*, 2007). This can be detrimental to the environment, the production resource base and to the consumers of the produce, (Alloway and Ayres, 1997 and Campos *et al.*, 2009).

Organisms acquire toxic substances from the environment along with nutrients and water. Some of the poisons are metabolized and excreted, but others accumulate in specific tissues. This capacity is widely recognized as offering one way of monitoring the distribution of toxins in the environment.

One of the reasons these toxins are so harmful is that they become more concentrated in successive trophic levels of a food web, a process called biological magnification (Campbell, 1996; Manly, 1996 and Kaonga *et al.*, 2010) Monitoring the distribution of toxins in the environment is important because it provides data required for planning, helps in the determination of the health and condition of a particular environment, provides a mean to record environmental changes and trends over time and finally it helps in focusing conservation efforts by relevant authorities towards decision making, (Roth *et al.*, 1997).

Heavy metals are general terms, which apply to the group of metals and metalloids with atomic density greater than 4 g/cm^3 , (Nriagu, 1999). This classification includes transition metals and higher atomic weight metals of group III to V of the periodic table. Heavy metals include lead, cadmium, zinc, copper, Iron etc (Duruibe *et al.*, 2007).

Heavy metals can be classified according to its health importance to: essential: Cu, Zn, CO, Cr, Mn and Fe. These metal also called micronutrients and are toxic when taken in excess of requirements, Non essential: as Ba, Al, Li and Zr, less toxic as Sn and Al and highly toxic as Hg and Cd. Heavy metals are also called trace element due to their presence in trace (10mg Kg⁻¹) or in ultra trace (1µg kg⁻¹) quantities in the environmental (Reeves and Baker, 2000).

The mechanism of toxicity of some heavy metals still remains unknown, although enzymatic inhibition, impaired antioxidants metabolism, and oxidative stress may play a role. Heavy metals generate many of their adverse health effects through the formation of free radicals, resulting in DNA damage, lipid peroxidation, and depletion of protein sulfhydryls (e.g., glutathione) (Valko *et al.*, 2005). The importance of these metals as environmental health hazards is readily evident from the fact that they ranked in the top 10 on the current Agency for Toxic Substances and Disease Registry Priority List of Hazardous Substances (ATSDR, 2005).

Heavy metals are toxic because they may have cumulative deleterious effects that can cause chronic degenerative changes (Ibrahim, *et al* 2006), especially to the nervous system, liver, kidneys, and, in some cases, they also have teratogenic and carcinogenic effects (IARC, 1987).

They are widely distributed in the earth's crust, but present at very low concentrations in the body. Their presence in the atmosphere, soil, and water, even in traces, can cause serious problems to all organisms. Their main impact on human health is principally through occupational exposure, environmental contamination, and accumulation in food, mainly in vegetables grown on contaminated soil. Arsenic and cadmium,

in addition to mercury and lead, have been identified as the most probable causes of heavy metal-related disease observed in primary care medicine (Hu, 2000). he added that exposure to one heavy metal contaminant is often accompanied by exposure to others. It is, therefore, expected that joint interactions may occur in populations exposed to mixtures of metals

The presence of heavy metals in the environment is one of the major concerns because of their toxicity and threat to human life. They accumulate in living tissues throughout the food chain which has humans at its top. These toxic metals can cause accumulative poisoning, cancer, and brain damage when found above the tolerance levels. (Al-Garni, 2005) .

Several investigations of water, soil and vegetables from urban areas have shown that these heavy metals are the main pollutants particularly of lands under irrigation with waste waters (Mohsen and Mohsen, 2008). heavy metal contamination of vegetables may also occur due to irrigation with contaminated water (Sinha *et al.*, 2006).

Heavy metals are among the major contaminant of food supply and are considered as problem to the environment (Zaidi *et al.*, 2005). heavy metals contamination may occur due to irrigation with contaminated water, the addition of fertilizers, metal based pesticides, industrial emissions, transportation, harvesting process and storage. Advancement in technology has lead to high levels of industrialization leading to the discharge of effluent bearing heavy metals into our environment. The various activities by man in recent years have increased the quantity and distribution of these heavy metals in the atmosphere, land and water bodies (Gustar, 1974).

In developing countries such as Kenya, rapid and unorganized urban and industrial developments have caused elevated levels of heavy

metals in the urban environments (Khillare *et al.*, 2004 and Sharma *et al.*, 2008a).

Heavy metals are non-biodegradable and persistent environmental contaminants, which may be deposited on the surfaces and then absorbed into the tissues of vegetables. Plants take up heavy metals by absorbing them from deposits on the parts of the plants exposed to the air from polluted environments as well as from contaminated soils (Sharma *et al.*, 2008b). a number of studies have shown heavy metals as important contaminants of vegetables (Singh and Kumar, 2006).

Emissions of heavy metals from the industries and vehicles may be deposited on the vegetable surfaces during their production, transport and marketing (Sharma *et al.*, 2008b).

There are many sources of trace metals contaminants that can be accumulated in soils. The burning of fossils fuels, smelting and other processing techniques release into the atmosphere which can be carried for miles and later deposited on the vegetation and soil. Lead, nickel and boron are gasoline additives that are released into the atmosphere and carried to the soil through rain and snow (Igwe *et al.*, 2005).

Dietary exposure to heavy metals has been identified as a risk to human health through the consumption of vegetable crops. The levels of Lead (Pb), Cadmium (Cd) and Chromium (Cr) in the tissue of *Talinum triangulare*, an economic plant grown around a textile industry in Ikorudu area of Lagos State was carried out in study. Two soil and plant samples each were collected from four different points. Three of the points were around the textile industry while the fourth was from a non-industrial area. The soil and plant samples were analyzed for Pb, Cd and Cr using Atomic Absorption Spectrophotometry (AAS). The levels of Pb (10.89 ± 4.69) and Cd (0.81 ± 0.01) in soil from the industrial area were higher than the non-industrial area (Pb) 2.33 ± 0.01 and (Cd) 0.65 ± 0.08 at

level $P < 0.05$. The same trend was recorded for the plant samples from the industrial and non-industrial area. These results suggest that contamination is due to industrial activities. This study further confirms the increased danger of growing vegetables around industries and if it is allowed to continue may lead to health hazard on part of consumers of the crop on the long term. This calls for proper monitoring and enforcement of industrial regulations by regulatory agencies (Akinola *et al.*, 2008).

Wastewater network levels for lead recorded for Melbourne in 1995 and 2006 were in a similar range of 4 -31 $\mu\text{g/L}$ (Connor and Wilkie, 1995), however the mean values were lower 13 $\mu\text{g/L}$ compared to 4.6 μg . in domestic residences, the laundry and the bathroom were identified as the main sources (Gray and Becker, 2002). The range at households varies widely. Dirt and dust from emissions and residues from lead based paints are suspected as the major inputs. Data from the UK also suggests a strong contribution from household infrastructure and faeces. However, lead pipe infrastructure is less common in Australia.

Prolonged consumption of unsafe concentrations of heavy metals through foodstuffs may lead to the chronic accumulation of heavy metals in the kidney and liver of humans causing disruption of numerous biochemical processes, leading to cardiovascular, nervous, kidney and bone diseases (Jarup, 2003; Codex Alimentary Commission (FAO/WHO, 2001).

Some heavy metals such as copper, cadmium, zinc, manganese, cobalt and Molybdenum act as micronutrients for the growth of animals and human beings when present in trace quantities, whereas others such as Cd, As, and Cr act as carcinogens (Trichopoulos, 1997 and Feig *et al.*, 1994), and Hg and Pb are associated with the development of abnormalities in children (Pilot and Dragan., 1996). Monitoring and

assessment of heavy metals concentrations in the vegetables from the market sites have been carried out in some developed and developing countries (Jassir *et al.*, 2005.; Radwan and Salama, 2006)

Ashokkumar *et al.* (2012) reported that the heavy metals viz. Zinc, Manganese, Nickel, Copper, Chromium, Cadmium, Lead and Cobalt in the waste samples. The metal zinc was measured in maximum extent in all the samples. The metals Zn, Mg, Ni, Cu, Cr, Cd, Pb and Co were measured minimum 0.45 mg/l, 0.28 mg/l, 0.021 mg/l, 0.005 mg/l, 0.018 mg/l, 0.001 mg/l and 0.002 mg/l and maximum 11.9 mg/l, 55.5 mg/l, 7.6 mg/l, 6.503 mg/l, 8.56 mg/l, 8.56 mg/l, 8.56 mg/l and 0.905 mg/l respectively. The heavy metals in waste can pose serious health problems in human also. It is recommended that periodic analytical testing of heavy metal should be carried out for maximum permissible level. Primary treatment is required for the quality of the waste/effluent.

Human health studies have addressed blood lead levels in children and urinary cadmium excretion in adults (Idaho Department of Health and Welfare Division of Health, 2000). Blood lead and urinary cadmium levels were elevated relative to those in reference populations. Similarly, a survey of wildlife in the vicinity of a zinc smelter site reported higher concentrations of cadmium in kidney and lead in bone than seen in animals from a relatively uncontaminated area, but did not address potential interactions among the studied components Cd, Pb, Zn, and Cu (Storm *et al.*, 1994).

A study of a ternary mixture of cadmium, lead, and zinc study in rats found slightly more marked adverse hematological effects with ternary mixture exposure than with binary mixtures (Thawley *et al.*, 1977). However, inconsistencies in dietary levels of calcium and vitamin D in this study made comparisons problematic. A well-controlled rat

study has reported protective effects of high dietary levels of zinc against some of the testicular effects of a mixture of cadmium and lead (Saxena *et al.*, 1989).

In a study (Fowler and Mahaffey, 1978), The data regarding interactions of arsenic, cadmium, lead, and zinc, are not adequate for predicting the magnitudes of interactions. Experimental efforts to identify interactions between these metals are needed. For some endpoints, the data are not robust in showing whether the joint action will be additive or greater or less than additive. In this case, the default approach (assumption of dose additive for individual components) is often used. This approach, which involves calculation of a hazard index, is most appropriate for chemicals that produce the same effects by similar modes of action.

Exposure to some of the elements, such as cadmium, lead, and arsenic, may vary from site to site. The toxicity data for a mixture containing these components in a fixed proportion might not be fully applicable to site assessments involving different proportions. Some judgment as to whether the mixtures are sufficiently similar would need to be made. When adequate health effects data on the same or a similar mixture are lacking, health effects data for the components of the mixture, along with data regarding interactions, are to be used for risk assessment (U.S. EPA, 1989). If adequate quantitative data on interactions of the components are available, the data would be used to predict the pattern of the interactions for various proportions of the mixture components or to modify the risk assessment, but such data may be difficult to obtain. For example, *in vitro* studies showed that chromosome mutagenicity resulting from coexposure to arsenic and antimony was sub additive, causing less cell damage than would an additive effect from the two metals (Gerbel, 1998). However, it may be

difficult to validate lab data in the absence of comparable field (epidemiological) data (McCarty *et al.*, 2004).

Cadmium (Cd) is a non-essential element that negatively affects plant growth and development. Cd density 8.6 g is a widespread heavy metal, can be released into the environment by mining, smelting activities, atmospheric deposition from metallurgical industries, power stations, heating systems, land application of sewage sludge, waste incinerators, burning of fossil fuels, urban traffic, cement factories and as a by-product of phosphate fertilizers. It is widely used in electroplating pigments, plastic stabilizers and nickel- cadmium batteries (Sanita and Gabrielli, 1999 and Tang *et al.*, 2006). It is recognized as an extremely significant pollutant due to its high toxicity and large solubility in water (IARC, 1993a).

The primary use of cadmium, in the form of cadmium hydroxide, is in electrodes for Ni–Cd batteries. Because of their performance characteristics e.g. high cycle lives, excellent low- and high-temperature performance, Ni–Cd batteries are used extensively in the railroad and aircraft industry (for starting and emergency power), and in consumer products (e.g. cordless power tools, cellular telephones, camcorders, portable computers, portable household appliances and toys) (ATSDR, 2008 and USGS, 2008).

The element cadmium is chemically similar to zinc and is found in soils and in deposits of zinc, copper and lead ores. Environmental pollution with cadmium has been taking place for several thousand years. Man started to produce metals from ores that happened to contain cadmium. However, the toxicity of cadmium has only been recognized for a relatively short time –since the 1970's (Nordberg *et al.*, 2007).

In occupational settings, cadmium and cadmium compounds, being non-volatile, exist in air as fine particulates. Animal studies (Rusch *et al.*, 1986) have shown that lung retention may be up to 20%, especially after short-term exposure. Humans absorb 5 – 10 % of ingested Cd, but a low intake of calcium, zinc or iron increases the degree of absorption. Subjects who are iron-deficient, for example, may absorb an increased proportion of the Cd they ingest (principally from food, water and tobacco smoke). Low level exposure will never actually be excreted from the body. Absorbed cadmium is excreted very slowly, and the amounts excreted into urine and faeces are approximately equal (Kjellström and Nordberg, 1978).

In humans, half-life estimates are in the range of 7–16 years, (Nordberg *et al.*, 2007). No essential physiological function has been proposed for Cd. However, it has physico-chemical similarities to zinc, which allow Cd to compete with zinc as a co-factor for zinc-dependent enzymes such as alkaline phosphatase, (Ellinder and Piscator, 1978), resulting in reduced activity of those enzymes. Cd also has transitional metal activity and can thus promote oxidative reactions in the tissues in which it has been sequestered. Cd particularly accumulates in the bone and the kidney, but its adverse health effects can now be demonstrated in almost every organ and tissue where it accumulates.

The primary symptom of prolonged exposure to high-dose cadmium is weak, brittle bones with spinal and leg pain “Itai Itai disease”, (Gallagher *et al.*, 2008). Human exposure to low levels of Cd can result in renal damage, osteomalacia, and lung cancer, as well as damage the cardiovascular system, liver, and reproductive system, (Hrudey *et al.*, 1995 and USEPA, 1992).

Nordberg *et al.*, (2007) reported that, environmental exposure to cadmium decreases bone density indirectly through loss of calcium in the urine as a result of renal tubular dysfunction. Other complications include anemia and renal failure. Cadmium at lower levels of exposure has been linked to osteoporosis, particularly in post-menopausal females, (Gallagher *et al.*, 2004).

Cadmium has an extremely long biological half-life (>20 years) and is listed as one of the 126 priority contaminants by the US-Environmental Protection Agency and as a human carcinogen by the International Agency for Research on Cancer (IARC,1994).

Cadmium does not break down in the environment. Atmospheric cadmium compounds are transported (sometimes for long distances) and deposited (onto surface soils and water) with minimal transformation in the atmosphere (ATSDR, 2008).

Mean total cadmium concentrations in air vary according to proximity to industrial source, and to population density. Measurement data from northern Europe for the period 1980–88 were reported as being around 0.1 ng/m³ in remote areas, 0.1–0.5 ng/m³ in rural areas, 1–10 ng/m³ in urban areas, and 1–20 ng/m³ in industrial areas, with levels up to 100 ng/m³ being observed near emission sources (WHO, 2000). Similar variations were observed in the USA (UNEP, 2008).

Cadmium is deposited in the soil by air pollution and absorbed by leaves and roots of plants, entering the food chain. Amounts inhaled by humans are small, less than 0.01, 0.2 and 0.4 µg/d in rural, urban and industrialized areas respectively Also Cadmium concentrations in drinking water overseas are usually very low between 0.01–1 µg/L

(WHO, 2000). Whilst in major Australian reticulated supplies concentrations of cadmium are usually less than 2µg/L.

The estimated average Australian adult dietary intake of cadmium is approximately 30 µg/day, with between 93-97% excreted through faeces (NHMRC, 2004). By comparison, European dietary intake is 15-25 µg/person/day on average (WHO, 2000).

Baker *et al.* (1990) reported that Cadmium never occurs in isolation in natural environments, but mostly as a 'guest' metal in Pb/Zn mineralization. Wagner (1993) estimated That polluting soil solutions contain cadmium concentrations ranging from 0.04 to 0.32µM. High concentrations of cadmium in soils (varying from 0.32µM to about 1µM) represent a potential threat to human health because it is incorporated in the food chain mainly by plant uptake, (Alvarez, 2008). Influence of cadmium toxicity on germination and growth of some common trees were investigated by (Iqbal and Mehmood, 1991).

The element cadmium is fairly immobile element, its accumulations in soils can become dangerous to all kinds of organisms. The increasing influx of heavy metals into water bodies from industrial, agricultural, and domestic activities is of global concern because of their well documented negative effects on human and ecosystem (Mataka *et al.*, 2006).

Cadmium is heavy metal with high toxicity and has an elimination half-life of 10-30 years. People are exposed to cadmium by intake of contaminated food or polluted air , (Jarup *et al.*, 1998). Cadmium is non-essential but poisonous for plants, animals, and humans (Gupta and Gupta, 1998).

In plants, Cadmium inhibits root and shoot growth, affects nutrient uptake and homeostasis, and frequently is accumulated by agriculturally

important crops. Cadmium is consumed by animals and humans in their diet and can cause diseases (Belimov *et al.*, 2005). Moreover, the normal level of cadmium in blood is under $5 \mu\text{g L}^{-1}$ but acute toxic effects observed when this level exceed $50\mu\text{g L}^{-1}$ (Pais and Jones, 1997). However, in case of Cadmium placenta acts as a fairly effective barrier and hence the new born are virtually free of cadmium. It was also shown that accumulation in the body increases with age and at the age of 50, non-occupationally exposed people may have 10-50 mg body burden of cadmium (Krausma and Lembit, 2004).

Inhalation is the major route of cadmium exposure in occupational settings, whereas most people in the general population are exposed to cadmium via the ingestion of both food and drinking-water. Exposure to cadmium particulates lead to cadmium absorption in animals and humans (IARC, 1993b).

When ingested, most of the cadmium passes through the gastrointestinal tract without being absorbed. Estimates of the cadmium absorption rate in humans have been reported as 3–5% (Morgan and Sherlock, 1984), or 6.5% (Horiguchi *et al.*, 2004).

When absorbed, cadmium will bind to metallothionein, forming a cadmium–metallothionein complex that is transferred (via blood) primarily to the liver and the kidney, Metallothionein is inducible in different tissues (e.g. liver, kidney, intestine, and lung) by exposure to various agents including cadmium (Waalkes and Goering, 1990). When transported to the kidney, cadmium–metallothionein is readily filtered at the glomerulus, and may be efficiently reabsorbed from the filtrate in the proximal tubules (Foulkes, 1978; Dorian *et al.*, 1992a). In the tubules, the protein portion is rapidly degraded to release cadmium (Dorian *et al.*, 1992b). Cadmium accumulates in kidney tubules, and causes damage to

tubular cells, especially in the proximal tubules, (Kasuya *et al.*, 1992) . The excretion process can itself cause renal tubular damage. However, as the reported age-related accumulation of Cd in the body (Elinder *et al.*, 1985).

Accumulating evidence also links environmental exposure to cadmium with an increased incidence of cancer affecting many different organs. For example, prospective studies in Japan and the United States have shown that excess cancer mortality is associated with environmental exposure to cadmium (Nishijo *et al.*, 2006). A Swedish study in 2008 reported increased endometrial cancer risk among participants in a cohort who consumed > 15 µg/day of cadmium, mainly derived from cereals and vegetables (Åkesson *et al.*, 2008).

There are many other current studies in the literature linking cadmium and cancer in non-occupationally exposed populations and, overall, these findings suggest a very large adverse health effect from exposure to cadmium at low levels of intake. Recent epidemiological studies also link exposure to Cd with effects in newly identified target organs. Cadmium exposure has been linked to diabetes, (Edwards and Prozialeck, 2009), diabetic nephropathy (Haswell, *et al.*, 2008), hypertension (Eum *et al.*, 2008), peripheral artery disease, (Navas *et al.*, 2005), myocardial infarction, (Everett and Frithsen, 2008), diminished lung function (Lampe *et al.*, 2008), periodontal disease (Arora *et al.*, 2009) and age-related macular degeneration of the eye. Evidence from other studies has suggested causal relationships between cadmium exposure and all-cause mortality, as well as between cadmium exposure and excess cancer mortality. This suggests that cadmium is at least a co-morbidity factor in a number of conditions such as cancer of the lung, pancreas, breast, endometrial, prostate and bladder, (Erie *et al.*, 2007).

Because of its high rates of soil-to-plant transfer, cadmium is a contaminant found in most human foodstuffs, which makes the diet a primary source of exposure among non-smoking, non-occupationally exposed populations (Franz *et al.*, 2008 and European Food Safety Authority (EFSA, 2009). Vegetables grown using water from industrial effluents may therefore be especially rich in Cd, as will vegetables grown in city environments polluted with smoke from motor vehicles.

Thus, cadmium pollution attracts the most attention of environmentalists throughout the world. Contamination of soil with heavy metals affects the qualitative and quantitative structure of microbial communities, resulting in decreased metabolic activity and diversity (Giller and McGrath, 1998). Although many soil bacteria are tolerant to heavy metals and play important roles in mobilization of heavy metals.

Lead (Pb): Lead is a bluish or silvery grey soft metal with atomic number 82; atomic weight 207.19; specific gravity 11.34, melting point 327.5 °C and boiling point 1740°C. It is the most common industrial metal that has become widespread in air, water, soil and food. Lead is slightly soluble in water and is transported mainly through the atmosphere. It behaves like calcium in body and accumulates in bone, liver, kidney and other tissues. (Swarup *et al.*, 2005).

Lead is a main-group element in the carbon group with the symbol Pb (from Latin: plumbum). Lead is a soft, malleable poor metal. It is also counted as one of the heavy metals. Lead, at certain exposure levels, is a poisonous substance to animals as well as for human. It damages the nervous system and causes brain disorders. Excessive lead also causes blood disorders in mammals. Like the element mercury, lead is a neurotoxin that accumulate both in soft tissues and the bones. Lead

poisoning has been documented from ancient Rome, ancient Greece, and ancient China.

Metallic lead can be toughened by addition of small amounts of antimony, or a small number of other metals such as calcium. All isotopes of lead, except for lead-204, can be found in the end products of the radioactive decay of the even heavier elements, uranium and thorium. Powdered lead burns with a bluish-white flame. As with many metals, finely divided powdered lead exhibits pyrophoricity. Toxic fumes are released when lead is burned (Charles *et al.*, 1966).

Lead has been commonly used for thousands of years because it is widespread, easy to extract and easy to work with. It is highly malleable and ductile as well as easy to smelt. Metallic lead beads dating back to 6400 BCE have been found in Catalhoyuk in modern-day Turkey. (Heskel and Dennis, 1983).

The largest preindustrial producer of lead was the Roman economy, with an estimated output per annum of 80,000 t, which was typically won as a by-product of extensive silver smelting. (Callatay, 2005). Roman mining activities occurred in Central Europe, Roman Britain, the Balkans, Greece, Asia Minor; Hispania alone accounted for 40% of world production. (Hong *et al.*, 1994).

Lead concentrations in natural environments are generally low. It is found in rocks, coal and sediment as immobile lead salts of poor water solubility. It is commonly encountered in urban environments due to the pollution by alkyl lead additives via automobile fuel combustion. Industrial activities such as iron and steel manufacture, coal combustion and copper smelting are also important contributors to dispersion of lead

into the atmosphere (WHO, 2001). Additional anthropogenic sources include lead in plumbing and flashing, in solder at pipe joints in old houses, dust from lead based paint commonly used prior to 1980, batteries, release from ceramic glazes, cosmetics, alloys, cable sheathing, rust inhibitors, ammunition, glazes and plastic stabilizers (WHO, 2001 and NHMRC, 2004). Lead toxicity has been observed at nutrient solutions of 10mg Pb/L to plants and for higher organisms.

Lead exposure assessments have been based on its intake from food, water, or air. Possible routes for lead exposure are inhalation and swallowing. The four main sources of contamination of food are soil, industrial pollution, agricultural technology, and food processing. Worldwide, there are six sources that account for most cases of lead exposure: gasoline additives, food-can soldering, lead-based paints, ceramic glazes, drinking water pipe systems, and folk remedies (Markowitz, 2000). Lead contamination can be present in food due to storage and manufacture, eg. canned food and alcoholic drinks (WHO, 2004).

Lead is present in tap water as a result of dissolution from natural sources or from household plumbing systems containing lead in pipes. The amount of lead from the plumbing system that may be dissolved depends on several factors, including acidity (pH), water softness, and standing time of the water, (Moore, 1973). Food can be contaminated by naturally occurring lead in the soil as well as by lead from sources such as atmospheric fallout or water used for cooking.

The industrial activity is the major source of lead contamination in water. There are various industries those are pertaining lead such as pulp and paper, petrochemicals, refineries, printing, pigments, photographic

materials and explosive manufacturing, ceramic, glass, oil, metal, phosphate fertilizer, electronic, wood production, combustion of fossil fuel, forest fires, mining activities, sewage wastewater, automotive, coating, painting, storage batteries, aeronautical, alloy and steel industries (Jalali *et al.*, 2002 and Bahadir *et al.*, 2007).

There are many workers who are at serious risk of high lead exposure, particularly those workers in industries where activities as following are done, Spray painting of vehicles; Recovering lead from scrap or waste; Steel bridge maintenance; Brass, copper and lead foundries ; Radiator manufacturing and repair; Car or boat maintenance and Working with assay laboratories. (WorkSafe, 2006 ; Oregon, 2007 and HSE UK, 2009).

In Europe, primary lead sources have been identified as run-off, contributing >20% depending on traffic conditions, 30-80% from domestic and 2-20 % from commercial sources, with 20-40% not accounted for (Icon, 2001). Likewise, Gray and Becker (2002) estimated from world wide data that >75% of the total lead in the wastewater from domestic areas was attributed to storm water.

The total intakes and uptakes of lead from all sources are 29.5 and 12.5 mg/d, respectively, for children and 63.7 and 6.7 mg/d, for adults respectively, in urban areas (World Health Organization, 1987). The relative contribution of water to average intake is estimated to be 9.8% and 11.3% for children and adults, respectively. The total intake of lead from three of the four major sources air, food, and dust appears to have dropped significantly since the mid-1980s as a result of regulatory and voluntary actions to control lead from air (via gasoline) and food (via cans).

The national and international health authorities such as World Health Organization (WHO) try to control the level of lead emission from any sources are in the allowable concentrations. The latest information of the maximum contamination of lead level in drinking water from the United State Environmental Protection Agency (EPA) is 0.015 mg/l (Gurel *et al.*, 2005). While the Control Department (PCD) of Thailand recorded that, the highest levels of lead Pollution in drinking and ground water qualities are 0.05 mg/l and 0.2 mg/l for industrial effluent (Dwivedi *et al.*, 2008)

Depending on the source, the concentration, and the bioavailability of lead determined by the physical and chemical form of lead, the relative contribution of each source may vary considerably. Although important measures have been implemented in a number of countries to decrease environmental lead exposure such as the use of unleaded gasoline, removal of lead from paints, solder of canned foods, and glazed ceramics used for storage and preparation of food, it is still a major environmental health problem in specific communities and targeted high-risk populations. Even though safety standards of the WHO-OSHA for blood lead in workers have been established at 40 µg/dL, no safe level of lead exposure has yet been defined, as health risks associated with lead are found at ever lower doses.

The CDC statement concerning lead poisoning in young children redefined elevated blood lead levels as that ≥ 10 µg/dL and recommended a new set of guidelines for treatment of lead levels ≥ 15 µg/dL (CDC, 1991). However, it has been suggested that the criterion for elevated blood levels in children is too high in adults based on substantial evidence (Muntner *et al.*, 2005). Greater prevalence of iron deficiency in young

children also increases the gastrointestinal absorption of lead (Albbasi and Rajindra, 1998).

When lead is released into the environment, it accumulated in food chain and exist in the nature. Lead can cause the severe health hazard even in the trace concentration. For instance, lead is extremely toxic and can cause damage to the nervous system, kidney, and reproductive system. Moreover it is toxic to human via interaction with the sulfhydryl group of proteins, resulting in disruption of the metabolism and biological activities of many proteins and it also impairs hemoglobin synthesis (Sone *et al.*, 2009).

Lead binds with a number of lead-binding proteins, but their identity or function is not as well defined as that of other metal-specific proteins. The most studied lead-binding protein is the denatured lead-protein complex identified as the intracellular inclusion body occurring in cells, particularly in the liver and kidney in persons with high-level lead exposure. It has been suggested that lead-binding proteins may have a protective effect for lead (Goyer and Clarkson, 2001).

Lead enters the body primarily through inhalation, ingestion of lead containing dust and dermal contact (mainly as a result of occupational exposure). Once in the body, lead travels in the blood to soft tissues such as the liver, kidneys, lungs, brain, spleen, muscles, and heart. The body does not change lead into any other form. Once it is taken in and distributed to the organs, the lead that is not stored in the bones is eliminated slowly from the body by the kidneys and gastrointestinal tract; negligible amounts of lead are lost through perspiration. About 99% of the amount of lead taken into the body of an adult will leave in the waste within a couple of weeks, but only about 32% of the lead taken into the body of a child will leave in the waste, (Barry, 1975). Greater prevalence

of iron deficiency in young children also increases the gastrointestinal absorption of lead (Albbasi and Rajindra, 1998).

Absorption of lead increases with pregnancy. Pregnant women absorb up to 85% of the lead to which they are exposed. Research indicates that lead in pregnant women can cross the placenta, affecting children even before they are born. Maternal cord blood lead levels of 10 µg/dL to 15 µg/dL appear to be associated with an increase in premature births, reduced birth weight, decreased stature and inability to maintain steady posture. Studies show that babies exposed to lead before birth may have learning and behavior problems that can last a lifetime. High levels of lead exposure during pregnancy may cause harm to the fetus, including birth defects, brain damage, hearing loss or even death.

The total body lead, approximately 80–95% in adults and about 73% in children accumulate in the skeleton. The biological half-life of lead is approximately 16–40 days in blood and about 17–27 years in bones, (Rabinowitz *et al.*, 1976).

Lead in bone is considered a biomarker of cumulative exposure because lead accumulates in bone over the lifetime and most of the lead body burden resides in bone. Some of the lead can stay in the bones for decades; however, some lead can leave the bones and re-enter the blood and organs under certain circumstances, for example, during pregnancy and periods of breast-feeding, after a bone is broken, and during advancing age.

Blood lead levels as low as 2 µg/dL may not cause distinctive symptoms but are associated with decreased intelligence and slower neurobehavioral development in the form of cognitive language deficits. Many other effects can begin to occur at these low blood levels. Recent

studies suggest that lead absorption is harmful at any concentration and that no safe level of lead exposure exists (Canfield *et al.*, 2003).

Materials and methods:

A) Sampling:

Three samples are taken from wastewater of each three hospitals from three cities western of Tripoli (El-Zawia central hospital, Subrata teaching hospital, and Surman general hospital,).

Samples are collected during the maximal hospital activity period (8:00 a.m. to 3:00 p.m.) in special sterile glass containers to prevent

contamination with source of lead or cadmium. Samples are transferred directly to the laboratory to measure the amount of cadmium and lead using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Another six samples from each city are collected from general sewer system (Domestic and industrial wastewater) of the city from different location which used as comparison group.

B) Separation of sludge from the liquid part of wastewater:

Wastewater consists of the insoluble or suspended solids (sludge) and the soluble compounds dissolved in water, non aqueous samples are refrigerated upon receipt and analyzed as soon as possible.

In order to avoid deterioration or contamination of samples, sampling procedures and sample preservation are done according to Standard Methods for the Examination of Water and Wastewater (Eaton *et al.*, 1995).

Sample preparation and analysis

The content of heavy metals (cadmium and lead) in wastewater and sludge are determined by atomic spectrometric method according to Polish standard method: PN92/C04570.

Wastewater samples preparation and analysis:

1- ten ml of concentrated Nitric acid (69.7%) were added to 10 ml of wastewater samples this step is carried out to decrease the ph of wastewater to be less than 5.

2-Then mixture is heated up to 95.5⁰C (less than boiling degree) to ensure complete digestion of samples and reduce their volumes by evaporation to about 2ml.

3- Non-ionized water (20 ml) were added then samples were filtered through 0.45 mm membrane filter, receive the filtrate in a 50ml flask and then complete with non-ionized water.

4-Then samples were analyzed using Atomic Absorption Spectra 10Plus to detect lead and cadmium contents.

Sludge samples preparation and analysis:

1-Sludge samples were dried in room temperature and then grinded till obtaining a homogenous mixture.

2- One to two gm of dried sludge of samples were weighed by electronic balance.

3- Ten ml of diluted nitric acid (1:1 volume) were added and mixed well and kept in covered beaker to prevent evaporation of samples, then heated samples at 95.5°C for 10-15 minutes.

4- Samples were left until cooling then 5ml of concentrated Nitric acid (69.7%), was added and samples were covered and heated for 30 minutes, then the covers were removed and left the solution to evaporate, reducing its volume by heating up to 2 hours without reaching to boiling point till the sample volume be about 5 ml.

5-After cooling of samples we added 2ml distilled water and 3ml of Hydrogen peroxide H_2O_2 (30%), then we covered samples and heated for about 5 minutes.

6-Then we added H_2O_2 , 1ml each time till no reaction were observed then we removed the covers and continue heating and evaporating reducing its volume by heating up to 2 hours without reaching to boiling point till the sample volume be about 5 ml.

7-The samples were left to cool then we added 10ml of concentrated Hydrochloric acid HCL (37%) and heated for 15 minutes at 95.5°C, samples were cooled and filtrated through 0.45 mm membrane filter,

receive the filtrate in a 50ml flask and then complete with non-ionized water.

8-Then samples were analyzed using Atomic Absorption Spectra 10 Plus to detect lead and cadmium contents.

Standard samples for each metal were also prepared according to the standard method. All tests are carried out in triplicates and their mean value is considered as the final result. Calculations are carried out using a computer program, Microsoft Excel 97 (Microsoft Inc.,USA).

Statistical Analysis:

The analysis of data was carried out by General Linear model. While , Duncan Multiple test was used to test the differences among means (SAS, 2002). The model used for studying the effects of the region; source of the element and the interaction between them on estimated lead and cadmium levels was as follows:

$$Y_{ijk} = \mu + R_i + S_j + (RS)_{ij} + e_{ijk}$$

Where:

Y_{ijk} = The trait of study;

μ = The overall mean;

R_i = The effect of region;

S_j = The effect of source;

$(RS)_{ij}$ = The effect of interaction between region and source and

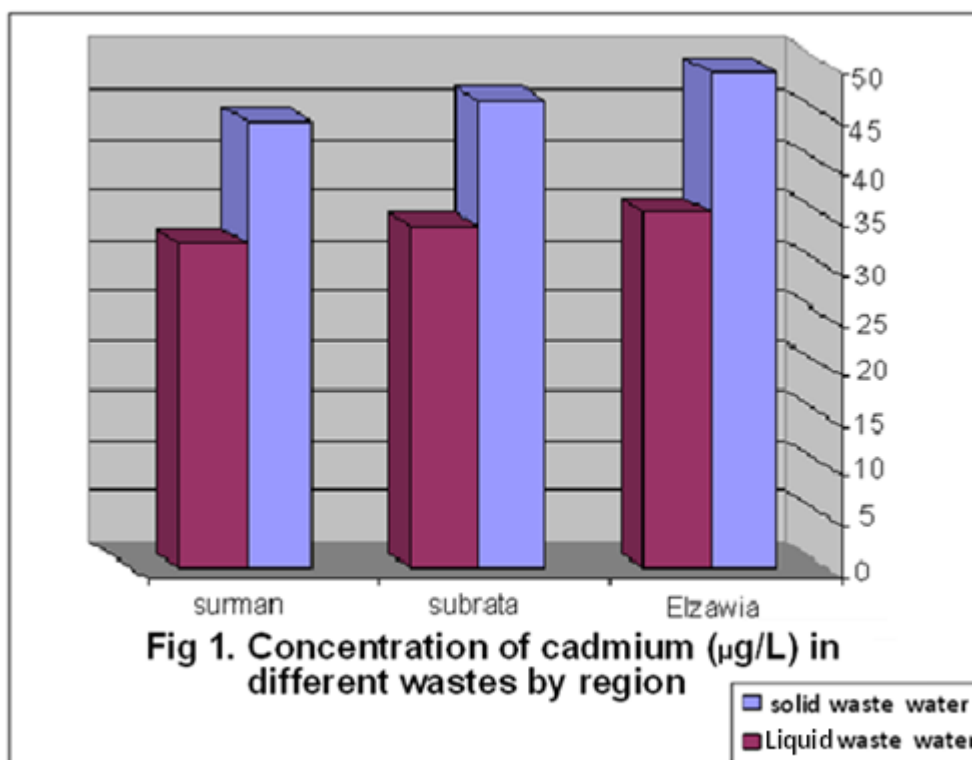
e_{ijk} = Random error.

Results

Generally, The concentration of cadmium in solid wastewater was higher than in liquid wastewater in all the samples tested. Also, the highest values for different wastewater found in El-Zawia region followed by Subrata and Surman regions, respectively (figure, 1).

The average of cadmium in solid wastewater were 49.11 ± 14.97 ($\mu\text{g/L}$) in El-Zawia region followed by values of 46.44 ± 14.69 and 44.22 ± 14.32 ($\mu\text{g/L}$) for Subrata and Surman regions, respectively. Also,

the average of Cadmium levels in liquid wastewater were 35.22 ± 10.76 ($\mu\text{g/L}$) in El-Zawia region followed by values of 33.78 ± 10.62 and 32.11 ± 10.70 ($\mu\text{g/L}$) for Subrata and Surman regions, respectively.



Also, The concentration of lead in solid wastewater was higher than in liquid wastewater as same as the level of cadmium, the highest values for different wastes found in El-Zawia region followed by Subrata and Surman regions, respectively (figure 2).

The average of lead levels as solid wastewater were 117.44 ± 19.73 ($\mu\text{g/L}$) in El-Zawia region followed by values of 113.67 ± 19.76 and 111.67 ± 19.49 ($\mu\text{g/L}$) for Subrata and Surman regions, respectively and the average of lead levels in liquid wastewater were 84.56 ± 10.84 ($\mu\text{g/L}$)

in El-Zawia region followed by values of 81.44 ± 10.88 and 79.89 ± 10.72 ($\mu\text{g/L}$) for Subrata and Surman regions, respectively.

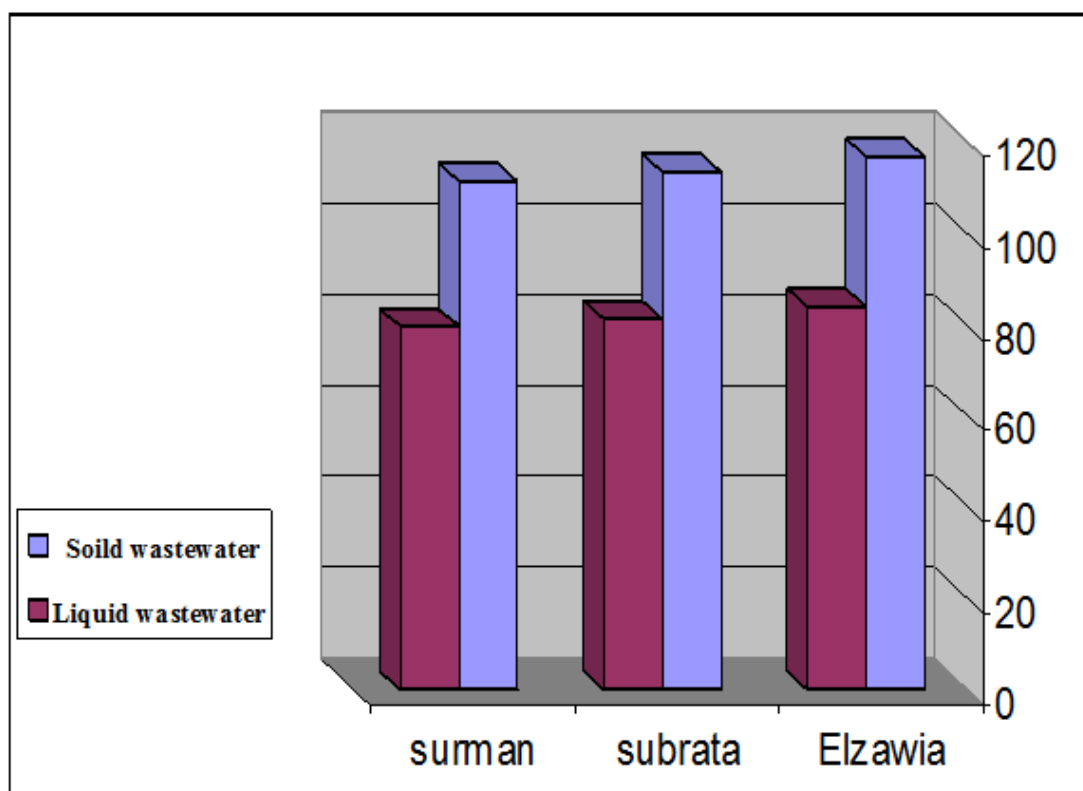


Fig 2. Concetration of lead (ug/L) in different wastes by region

In other hand, concentrations of cadmium depend on sources are shown in figure (3). In general, the concentration of cadmium in solid wastewater was higher than in Liquid wastewater and the highest values were found in Industry wastewater. The average of this element as solid wastewater was $104.67 \pm 2.11(\mu\text{g/L})$ in industry followed by values of 23.22 ± 1.10 and 11.89 ± 0.63 ($\mu\text{g/L}$) in hospital and Home wastewater , respectively. Moreover, the average of Cadmium levels as liquid wastewater was 76.22 ± 0.89 ($\mu\text{g/L}$) in industry followed by values of

16.00 ± 0.67 and 8.89 ± 0.56 ($\mu\text{g/L}$) for hospital and Home wastewater, respectively.

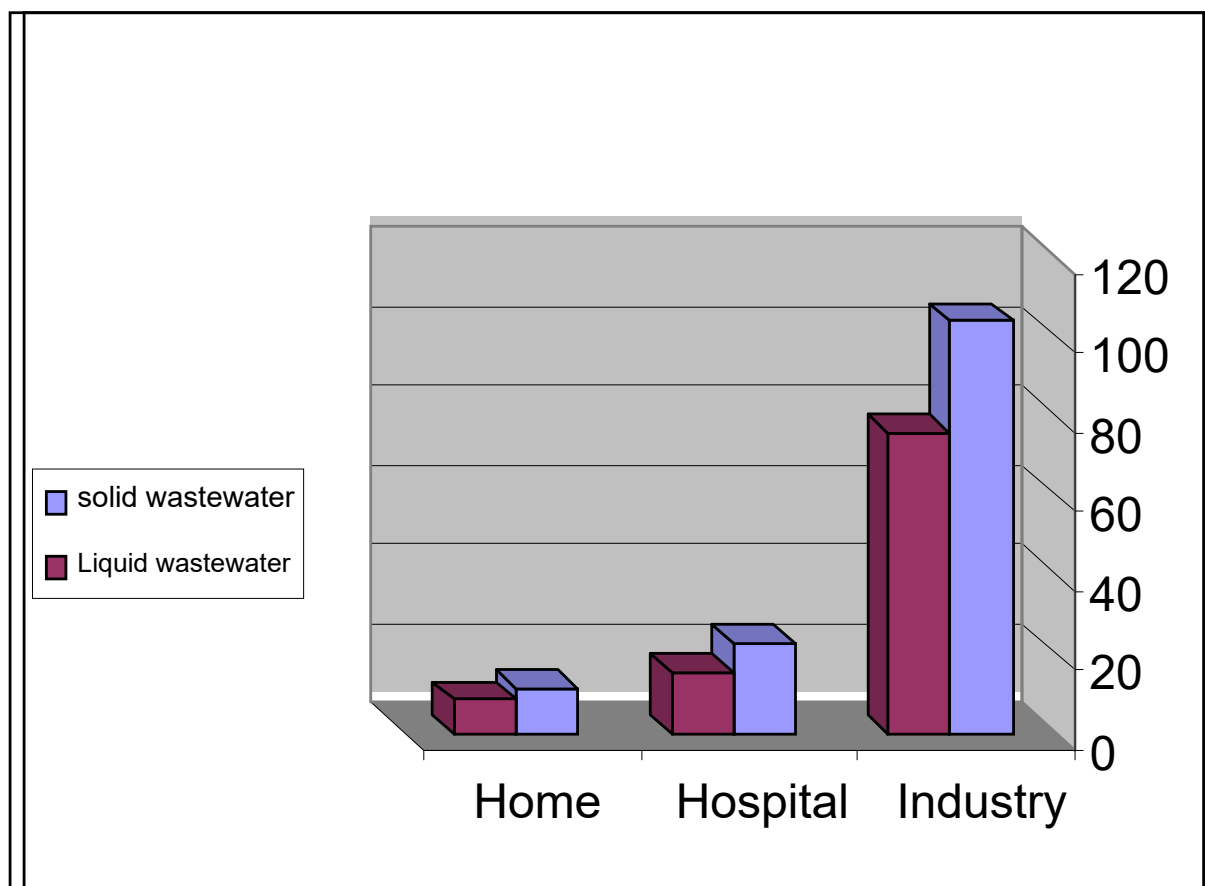


Fig 3. Concentration of Cadmium ($\mu\text{/l}$) in different wastes by sources

Concentration of Lead ($\mu\text{g/L}$) in different wastewater by sources are shown in figure (4). The concentration of Lead in solid wastewater was higher than in liquid wastewater and the highest values found in Industry followed by Hospital and Home sources as following values 186.33 ± 2.66 ($\mu\text{g/L}$) in industry and 104.33 ± 2.86 , 52.11 ± 1.52 ($\mu\text{g/L}$) in hospital and Home wastewater , respectively. in addition, the average of lead levels as Liquid wastewater were 118.89 ± 1.92 ($\mu\text{g/L}$) in industry

followed by values of 82.33 ± 1.67 and 44.67 ± 1.22 ($\mu\text{g/L}$) in hospital and Home liquid wastewater, respectively.

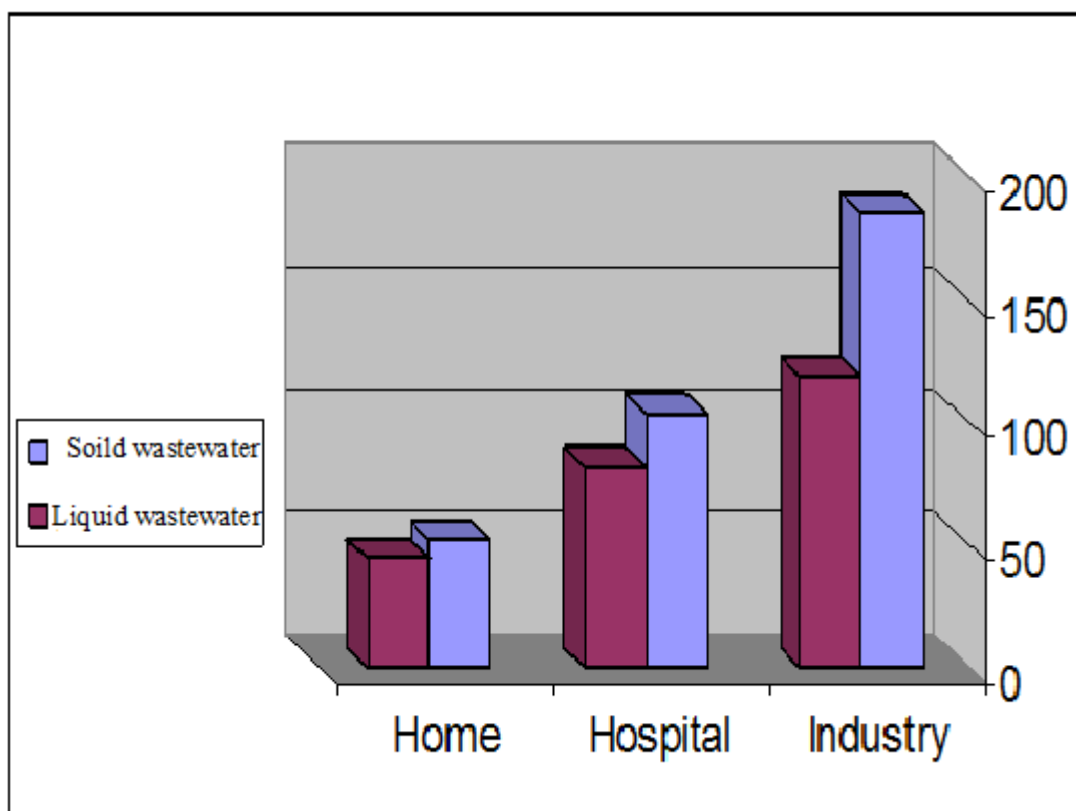


Fig 4. Concentration of Lead in different wastes by sources

Generally, The industrial wastewater had the highest values of solid and liquid wastewater for both lead and cadmium levels more than concentrations in both hospital and Home wastewater.

In other hand, El-Zawia city had the highest values of lead and cadmium levels in both solid and liquid wastewater compare to other two cities Surman and Subrata as shown in figures (5 and 6).

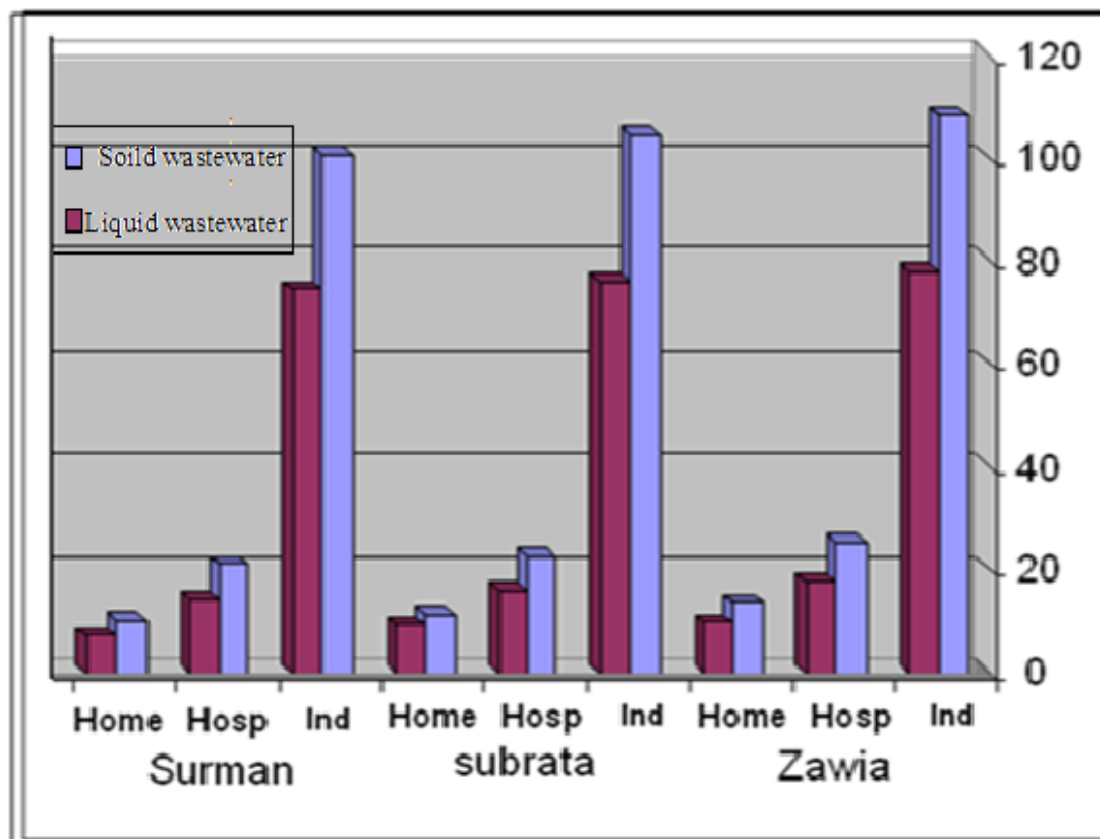


Fig.5: Concentration of Cadmium (ug/L) in different wastes and different cities and sources

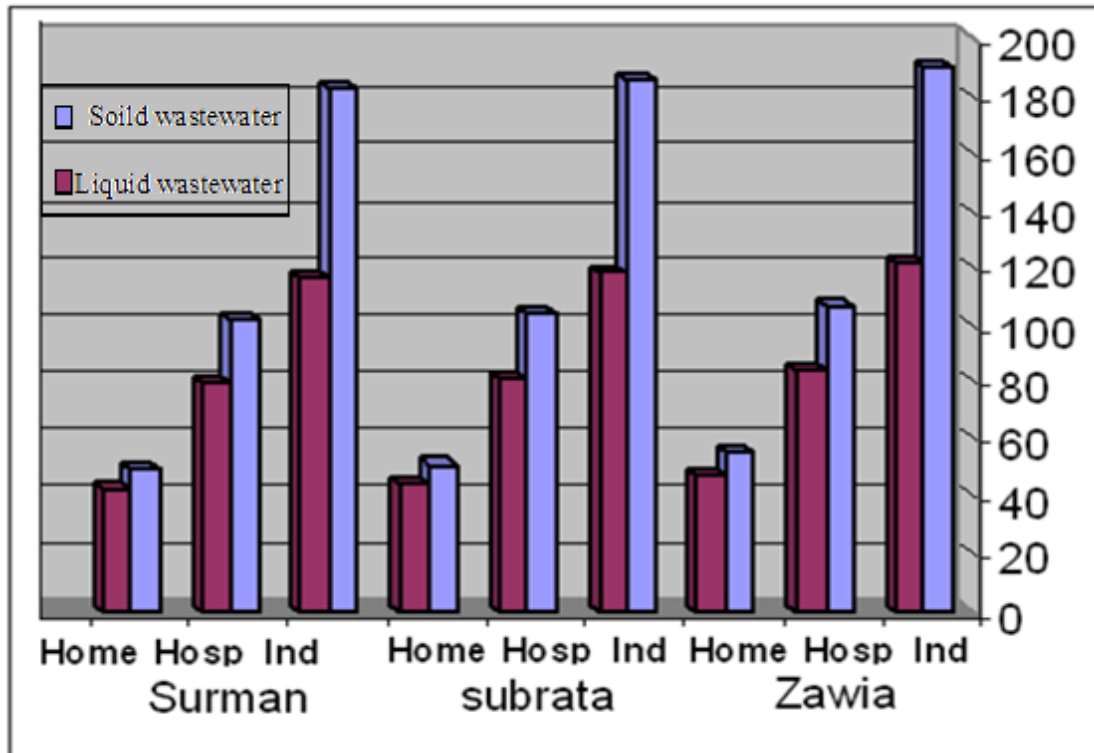


Fig. 6: Concentration of Lead (ug/L) in different wastes and different cities and sources

Discussion and Conclusion

Generally, The results in our study showed that both lead and cadmium concentrations ($\mu\text{g/L}$) are significantly elevated in wastewater;

either solid or liquid wastewater in all examined regions (El-Zawia, Subrata and Surman).

Generally El-Zawia shows the highest levels in comparison to Subrata and Surman cities (117.44 & 84.5 $\mu\text{g/L}$) for lead in sludge and liquid wastewater respectively, and for Cadmium were 49 & 35 $\mu\text{g/L}$ solid and liquid wastewater respectively. The El-Zawia city had, also, the highest values of solid and liquid wastewater for both lead and cadmium levels compare to Subrata and Surman cities which are related to the size of population of the city, the amount of industries activities in the city and the amount of traffic activities inside the city.

Also, it found that both lead and cadmium residues are significantly higher in industrial wastewater compared to hospital and home either solid or liquid wastewater. Sardar *et al.* (2002) agreed with our results in his study when he investigate selected steel and pharmaceutical industries for amount of Pb and Cd in wastewater, his results found as 1.50 mg/L and 0.06 mg/L in wastewater of Steel industries compare to wastewater for pharmaceutical industries, which were for Pb 0.6 mg/L and Cd 0.02 mg/L.

Another work by Omgbu and Kokogb (1993) Observed higher levels of Pb and Cd in soil from industrial area than non industrial area which confirm that contamination is due to industrial activities.

Olaniyi *et al.* (2012) observed that the levels of cadmium (1.47 ppm) and lead (16.26 ppm) in the wastewater samples were high when compared to the levels of other metals in the samples they attributed.

The high level of lead in the sample came from the parts of the equipment or machinery used at different stages of the production of the vegetable oil. The high levels of cadmium and iron in the samples can be

attributed to the presence of abandoned metal scraps at the site of the wastewater outlets. The high concentration of these metals could have adverse effect on the aquatic life and human in general. Also, Castro (1993) in his work go in parallel with stated that, high levels of heavy metals were found to be for Cadmium (5-43 $\mu\text{g/L}$) and lead (10 -253 $\mu\text{g/L}$) in industrial wastewater.

Yasser *et al.* (2011) examined the concentrations and distribution of heavy metals in the soils at three sites Shoubra al khima industrial zone with heavy traffic, Helwan industrial zone south Cairo, and rural area far from Cairo- Egypt. He found that high concentration of both Cd and Pb were related to the size of traffic activities followed by industries activities and less concentration were in rural area far from Cairo the capital. Soil represents a major sink for heavy metals ions, which can then enter the food chain via plants or leaching into ground water. The most important heavy metals with regards to potential hazards and the occurrence in contaminated soils are: Cd, Pb, and Zn. The concentration of these toxic elements in soils may be derived from various sources, including anthropogenic pollution, metal deposits, and agriculture as well as natural activities. Chemical and metallurgical industries are the most important sources of heavy metals in the environment

Yasser *et al.* (2011) in a study to determine heavy metals levels in areas in Egypt remarked that the concentration of all measured metals in the selected areas were significantly higher in the industrial area associated with high traffic density. This shows the extent to which this automobile and industries release those metals as pollutants into the environment. The results of the this study confirm that the main reason of high concentration of heavy metals localized in the industrial area is

either related to the industrial activities or the density of traffic which both two major factors found in El- Zawia compare to less activities area found in both other cities Subrata and Surman with low populations and fewer industries activities.

The recent environmental studies assessed the risk of hospital wastewater that based upon dilution, (Mcardell, *et al.*, 2010), to avoid extreme diversity of physical, chemical and biological evolutions lead to sanitary risk and could be dangers to the ecological balance and public health that require on-site treatment to prevent contamination the city's sewerage, (Gautam *et al.*, 2007).

The results in current study showed that hospital are important source for contamination of environment by wastewater contain heavy metals such as Pb and Cd. Ekhaise and Omavwoya (2008) showed that, the hospital wastewaters has some parameters whose values are higher than the WHO levels. Other falls within the WHO acceptable limits. The permissible limit of Cd and Pb are 0.01 mg/L and 0.05 mg/L, respectively, according to WHO (2004).

Therefore, contamination of the receiving environment (water, soil and air) due to the discharged hospital wastewater, which could probably be hazardous to human health.

The chemical substances used in hospitals for cares activities and for medical research are the more often recovered in the liquid sewages. Even though the raised volume of wastewaters, generated by these

establishments, assure an important dilution of the present pollutants, the dismissal of these sewages in the local purification network or in the nature represents a meaning full contribution to the general contamination

of environment, and more especially of the aquatic media. Indeed, the hospitals have been identified like an incontestable source of chemical compounds in the aquatic ecosystems. Contamination the most frequently met is made of micro - pathogenic organisms (of which some are multi resistant to antibiotics) and metals, (Leprat, 1998).

Domestic sources of potentially toxic elements in wastewater are rarely quantified due to the difficulty in isolating them. Domestic sources include the potentially toxic elements discharged from the household to Urban Waste Water (UWW) collecting systems and, in addition, corrosion from materials used in distribution and plumbing networks, tap water and detergents. (RIVM, 1993).

The maximum concentrations of potentially toxic elements found in commercial wastewater are generally greater than those in domestic wastewater, these results agreed with our results. Karanja *et al.* (2010) reported that, the heavy metal concentrations in the soils showed that lead was the highest in concentration followed by cadmium and chromium.

Naser, (1998) showed results similar to ours remarking significant increase in both Lead and Cadmium in wastewater even after treatment and he explained this increment to evaporation and contamination of treated wastewater.

From the results in current study, it can be said that there is an urgent need to raise awareness and education on wastewater management. Proper wastewater treatment strategy is needed to ensure health and environmental safety specially in Industries and health care sector which are the most polluter to our environment. General policy needed to insure

safety to eliminate the major source of heavy metals from pollute our environment.

Recommendations

In order to increase community awareness of lead and cadmium waste in Libya. There are several recommendations suggested in this study. These recommendations include:

1- Improve the education or training about heavy metals risks especially for people who live in rural areas where there is a lack of information and awareness about heavy metals risks such as lead and cadmium and other environmental diseases.

2- Improve wastewater management for the whole country. Wastewater may be a source for many hazardous materials, and consider one of the environmental problem in Libya.

3- Improve environmental policy. The current environmental policy needs to be improved by addressing the potential source of environmental hazards. For example, as mentioned previously, agricultural land should be separate from urban areas and traffic densities in order to eliminate lead contamination of vegetables. In order to manage farming areas, the government needs to urge businesses not to build close to farming areas.

4- Demand that the government regulate lead consumer products. This is important, especially since Libya has entered into free trade agreements

5- Additional studies should be undertaken to acquire additional and more detailed information about the waste burning and incineration and its consequences in Libya.

6- Cleaner production based on a circular vision of the economy should be encouraged.

7- Industrial estates can reduce community and environmental impacts by isolating potentially hazardous processes in areas far away from residential neighborhoods and by ensuring safety and environmental standards for all of the industries in the zone.

8- The study recommended that the hospitals have to select onsite separate wastewater treatment alternative. Indeed, efforts must be

undertaken by hospitals to integrate environmental control and safe program to avoid a higher risk safety factor of hospital facility operations.

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