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ESTIMATION OF SOME METALLIC POLLUTANTS EMITTED FROM SUPERPHOSPHATE INDUSTRY IN MILK AND SOME MILK PRODUCTS IN ASSIUT GOVERNORATE

(With 4 Tables)

By

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قياس لبعض الملوثات المعدنية المنبعثة من صناعة الأسمدة الفوسفاتية في اللبن وبعض منتجاته فى محافظة أسيوط

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يشكل التلوث الناتج عن مخلفات المصانع خطورة على صحة الإنسان وخاصة في الأماكن المأهولة بالسكان والتي تربى بها حيوانات انتاج الألبان. ولأن اللبن ومنتجاته من أهم وأكثر الأغذية استهلاكا للكبار والصغار، فإن تلوثها بمخلفات المصانع يعد مصدراً للتلوث الكيميائي. وتعتبر المعادن الثقيلة من أهم الملوثات الكيميائية التي تنبعث من الأنشطة الصناعية مثل صناعة الأسمدة الفوسفاتية. لذا فان تواجدها في اللبن ومنتجاته يلاقى اهتماما واسعا من قبل المهتمين بسلامة الغذاء. وعلى ذلك يجب الاهتمام بفحص الأغذية ذات الأصل الحيواني لتقدير تركيزات هذه العناصر بها لما لها من تأثير تراكمي يؤثر على صحة المستهلك. استهدفت هذه الدراسة تقديراً لبعض العناصر الثقيلة مثل الكادميوم و النحاس والفوسفور والكبريت والتي تعتبر من أهم المخلفات الناتجة من مصانع السوبر فوسفات. حيث جمع عدد ٩٣ عينة عشوائية من كل من اللبن الخام والجبن القريش والزبد الفلاحي، موزعة بالمناطق الآتية: ١) عزبة جودة الملاصقة لمصنع الأسمدة بمنقباد بمحافظة أسيوط، حيث تم جمع عدد ٤٣ عينة (٣٣ لبن، ٥ جبن قريش، ٥ زبد فلاحي) ، ٢) قرية منقباد والتى تبعد ١,٥ كم شمال المصنع، وتم تجميع عدد ٢١ عينة (٧ لبن، ٧ جبن قريش، ٧ زبد فلاحي)، ٣) من مدينة ديروط والتي تبعد ٥٣ كم شمال المصنع، فتم جمع عدد ٢٩ عينة (٧ لبن، ١٧ جبن قريش، ٥ زبد فلاحي). وتم إجراء الفحص الظاهري لجميع العينات ثم قياس مستوى كل من الكادميوم والنحاس باستخدام جهاز الامتصاص الذري، أما عنصري الفوسفور والكبريت فقد تم قياسهما بواسطة جهاز الأمتصاص الطيفي. وأظهرت النتائج أن هناك زيادة معنوية في مستوى تركيزات هذه المعادن الذي فاق المعدلات المسموح بها

عالميا. وكانت المتوسطات للكادميوم والنحاس والفوسفور والكبريت في اللبن في عزبة جودة كالتالي ٠,١، ٠,٤٤، ١١٦٠,١، ٤٤٠,٤ جزء في المليون علي التوالي، وكانت في قرية منقباد ٠,٠٩، ٠,٤٩، ١٠٩٣,٧، ٣٢٢,٥ جزء في المليون علي التوالي، وبمدينة ديروط كانت ٠,٠١، ٠,١٧، ٦٥٦,٩، ٢٩٣,٨ جزء في المليون علي التوالي. أما بالنسبة للجبن القريش فكانت ٠,٥، ١,٨٩، ٣٣٥٠,٠ ، ٤٠٥,٤ جزء في المليون علي التوالي بعزبة جودة و٠,١٥، ١,٤٩، ٣١٣٠,٠ ، ٣٧٧,٥ جزء في المليون علي التوالي بقرية منقباد، وكانت ٠,٠، ٠,٤١، ٢٨٤٨,٠، ٣٠٩,٢ جزء في المليون علي التوالي بمدينة ديروط. أما بالنسبة للزبد الفلاحي فكانت ١,٢، ٠,٩ ، ١٤٨٩,٢، ٤٢٠,٨ جزء في المليون علي التوالي بعزبة جودة و ٠,٠١، ٠,٤١، ١٣٠٦,٠، ٤٠٨,١ جزء في المليون علي التوالي بقرية منقباد ، و ٠,٠، ٠,٢٥، ١٠٩٠,٤، ٣٠٢,٠ جزء في المليون علي التوالي بمدينة ديروط. ومن هذه النتائج يتضح أن هناك زيادة معنوية في مستوى تركيزات جميع المعادن موضوع الدراسة مقارنة بالحد المسموح به من منظمة الصحة العالمية ومنظمة الأغذية والزراعة وبخاصة في العينات التي تم تجميعها من عزبة جودة وقرية منقباد ولم تكن هذه الزيادة معنوية بالعينات التي تم تجميعها من مدينة ديروط. مما سبق يتضح أن هناك نوع من التلوث البيئي ببعض العناصر الثقيلة والتي لها علاقة بنشاط المصنع موضع البحث. وعلى ذلك يستوجب مستقبلاً دراسة أوفى لمصادر التلوث والعمل بكافة الوسائل على إيقافها تجنبا لمخاطرها على صحة الإنسان والحيوان والبيئة المحيطة. هذا وقد تم مناقشة التأثير السمي لبعض العناصر الثقيلة وكذلك مناقشة الخطوات الواجب اتباعها للحد من تلوث الألبان ومنتجاتها بهذه العناصر.

SUMMARY

A factory producing phosphates fertilizer located in Manqabad village of Assiut governorate caused several heavy metals pollution to the surrounding environment through its discharge of industrial wastes and their recycling in soil and water resources. Lactating animals exposed to these pollutants through consuming contaminated grass, water and breathing contaminated air. This study aimed to estimate the levels of contamination in milk and some milk products with some metallic pollutants emitted from the factory. A total of 93 samples of raw milk, kareish cheese and cooking butter were collected from 3 different areas: 33 milk samples, 5 samples of kareish cheese and 5 samples of cooking butter were collected from Ezbet Gouda next to superphosphate factory at Manqabad village, Assiut governorate; 21 samples from Manqabad village which is about 1.5 km north to the factory, (7 milk, 7 kareish cheese and 7 cooking butter); 29 samples from Dayrut city which is about 53 km north to the factory, (7 milk, 17 kareish cheese and 5 cooking butter). All samples were examined physically for color and flavor. Cadmium (Cd), copper (Cu), phosphorous (P) and sulfur (S) concentration were also measured. The levels of Cd, Cu, P and S concentrations in milk samples were 0.1, 0.44, 1160.1 and 440.4 ppm in

Ezbet Gouda; 0.09, 0.49, 1093.7 and 322.5 ppm in Manqabad village and 0.01, 0.17, 656.9 and 293.8 ppm in Dayrut city, respectively. Levels of such elements in kareish cheese samples were 0.5, 1.89, 3350.0 and 405.4 ppm in Ezbet Gouda; 0.15, 1.49, 3130.0 and 377.5 ppm in Manqabad village and 0.0, 0.41, 2848.0 and 309.2 ppm in Dayrut city, respectively. The levels of such elements in cooking butter samples were 1.2, 0.9, 1489.2 and 420.8 ppm in Ezbet Gouda; 0.01, 0.41, 1306.0 and 408.1 ppm in Manqabad village and 0.0, 0.25, 1090.4 and 302.0 ppm in Dayrut city, respectively. The obtained results showed a significant increase in Cd, Cu, P and S levels than the maximum acceptable limits (MAL) especially in Ezbet Gouda next to the factory then in Manqabad village, while, that increase was not significant in Dayrut city. The geographical distribution of such increase suggested the possibility of the metallic pollution of milk and milk products in the surrounding zone to the factory. This work recommend the regular monitoring of these products to alarm about the degree of pollution and to protect the consumers from the toxic hazards of these contaminants on their health.

Key words: *Metallic pollutants, Superphosphate industry, Milk, Kareish cheese, Cooking butter*

INTRODUCTION

Environmental pollution is considered one of the major threaten to animal and human health. This pollution accompanied with various human activities. Industrial activities in multiple types of factories represent the most dangerous source of this pollution. These factories are responsible for contamination of the surrounding environment with several pollutants (Okada *et al.*, 1997). The emission of some metallic pollutants to the surrounding environment from the superphosphate factories represents the main source of industrial pollution in these areas (Shehata *et al.*, 1989).

Heavy metals including essential and non-essential elements are used extensively in the industry. These metals may contaminate the food source by leaching process from soil and water bodies leading to contamination of the animal feed. Dairy cattle and buffaloes present in metallic polluted areas were greatly affected and produced contaminated milk with various types of pollutants (Carl, 1991). Milk is a food rich with oligoelements that can vary in concentration due to genetic factors, type of feed, in addition to, the contamination in the area of production. Since the margin between the concentration of mineral requirements and the toxic levels is so narrow that a little excess results harmful to sensitive species (Higham and Tomkins, 1993). The mineral elements can be divided into macro minerals (major elements) and micro minerals (trace elements). The macro minerals such as sodium (Na), magnesium (Mg), calcium (Ca) and P are required to the body in amounts greater than 100 mg/day whereas the micro minerals such as iron (Fe), Cu, zinc (Zn) and manganese (Mn) are required in amounts less than 100 mg/day (Murray *et al*., 2000).

Cadmium and its salts are widely employed in numerous industrial processing and it is a component of many commercial products. It is obvious from animal, clinical and/or industrial studies that Cd is a potent metal toxicant. Cd is also considered one of the dangerous metal contaminants of food and drinks due to its wide distribution and numerous industrial highly valued uses in modern technology. It was presumed to be a possible source of environmental pollution through galvanized pipes, effluents from electroplating works and geological deposits (Dwivedi *et al*., 1997 and Melgar *et al*., 1997). Human exposure to Cd may result from both occupational and environmental sources and mainly through food (WHO, 1992). Food represents the second major source of exposure to Cd (Lee and White, 1983).

Long-term applications of phosphate fertilizers can lead to Cd accumulation in soils (Agbenin, 2006). Although, Cd is vitally absent from the human body at birth, it is highly cumulative poison with a biologic half-life of 20-30 years causing renal failure (Gracey and Collins, 1992 and Manahan, 1992).

Cd is known to induce chronic renal disease due to the fact that urinary elimination is the main route of excretion, and the proximal tubules are especially sensitive due to their higher absorptive activity (Madden and Fowler, 2000). Anemia is a common manifestation of chronic Cd toxicity due to its antagonism to Cu and Fe. In animals, chronic oral feeding of subtoxic doses of Cd salts leads to immunotoxic effects; reduction of neutrophil, macrophage and lymphocyte functions (Beisel, 1982). It is a potent and effective carcinogen in rodents and recently has been accepted by the International Agency for Research on Cancer as category 1 (human) carcinogen (IARC, 1994) based primarily on activity as pulmonary carcinogen (Stayner *et al*., 1992). It also plays a significant role in the cause of hypertension and osteomalacia (Friberg *et al*., 1989). In addition, Cd has been shown to affect the disposition and excretion of Cu and Zn in growing and adult animals (Mahaffey *et al.*, 1981 and Wesenberg *et al.*, 1981). As Cd its ubiquitous in nature, all food may exposed and contained it (Watson, 1993).

The provisional tolerance weekly intake (PTWI) of Cd in milk ranged from 0.005-0.05 ug/kg in different countries as recorded by Carl (1991). IDF (1991) reported that 0.00002-0.0008 mg/kg is the normal range of Cd in milk. According to WHO (1998) PTWI of Cd is 0.007 mg/kg/bw/ week for adults.

Copper is the third most abundant essential trace element in the body after Fe and Zn (Sarker, 1994). The total amount of Cu in the body of adults is 80-150 mg (Kruse-Jarres, 1994). This element is essential for the proper functioning of many enzymes including cytochrome C oxidase (energy production), superoxide dismutase (antioxidant protection), tyrosinase (pigment formation), dopamine hydroxylase (catecholamine production), lysyl oxidase (collagen and elastin formation), clotting factor V (blood clotting), ceruloplasmin antioxidant protection, Fe metabolism and Cu transport. (Sarker, 1994). Repeated Cu exposures have been associated with hemolytic anemia (Manzler and Schreiner, 1970). Both deficiency and excess of Cu in the mammalian system result in serious effects (Hostynek *et al.*, 1993). Abnormally high liver Cu levels lead to various diseases including Mediterranean anemia, hemochromatosis cirrhosis, yellow atrophy of liver and Wilsons disease "hepatocellular degeneration" (Underwood, 1977). In addition, its content in milk varies with the species, stage of lactation and Cu intake of dairy animal, although milk is considered the poorest source of Cu (not more than 0.3 ppm) as recorded by Underwood (1977) or less than 0.1 ppm as reported by Harrison (1993). Ibrahim *et al.* (1984) recorded Cu levels of 0.136 and 0.132 ppm in cow and buffalo's milk in Assiut city, respectively. While, CAC (1984) stated that Cu intake from food and drink not exceed 0.5 ppm/day.

Phosphorous is ranked as the second most abundant mineral element in the human body after Ca. About 80% of P is combined with Ca in bones and teeth where as the other 20% participate in body functions such as cell growth and contraction of the heart muscle (Passmore and Eastwood, 1986). The element is also an important component of adenosine tri-phosphate (ATP), phospholipids and nucleic acids (Peeley, 1998). Jensen (1998) reported that P together with Ca are mainly associated with the micelle structure of casein in milk. Fresh cow milk has been found to contain P as 93 mg/100g (Kataoka *et al.*, 1991). High P intake is detrimental to Ca absorption. The most common adverse reaction of high intake of P is hypocalcaemia even in healthy individuals with normal renal function (Knochel, 1999). Phosphates are used in fertilizers and as animal feed supplements. They are also used in the manufacture of industrial chemicals and pharmaceuticals and as detergent builders. High phosphate concentrations in surface waters may indicate fertilizer runoff, domestic waste discharge or presence of industrial effluents or detergents. If high P concentration persists, algae and other aquatic plant life will flourish eventually causing decreased dissolved oxygen levels in the water due to the accelerated decay of organic matter. P measurement is used to control scale and corrosion inhibitor levels in boilers and cooling towers. It was reported that P contributes to increase eutrophication of surface water through a process that increases algae growth and disrupts the ecosystem of the water resulting in increased fish losses (Sharpley *et al.*, 1994). Excess P may also cause toxic algal blooms that may be dangerous to human health (USDA, 1999). In an effort to curb these detrimental effects, USDA (1999) has established that most animal feeding operations must develop a comprehensive nutrient management plan. Morse *et al.* (1992) showed that P excretions by lactating cows were increased. Acceptable daily intakes (ADI) of P set by FAO/WHO (1989) committee are fixed at 30 and 70 mg/kg/bw. In light of the increasing application of phosphates in food industries, the question arises whether these permissible limits are not exceeded by certain population group (El-Shaarawy and Reith, 1979).

Sulfur has many industrial uses such as in batteries, detergents, the vulcanization of rubber, fungicides and in the manufacture of phosphate fertilizers (Lid, 1993). The burning of coal and petroleum by industry and power plants creates massive amounts of sulfur dioxide (SO_2), which reacts with atmospheric water and oxygen to produce sulfuric acid. This sulfuric acid is a component of acid rain, which lowers the pH of soil and freshwater bodies resulting in substantial damage to the natural environment and chemical weathering of statues and structures (Lid, 2007). S is an essential component of all living cells. It may serve as chemical food source for some primitive organisms and it is absorbed by plants via the roots from soil as the sulfate ion and reduced to sulfide before it incorporated into cysteine and other organic S compounds. In plants and animals the amino acids cysteine and methionine contain S, as do all polypeptides, protein and enzymes which contain these amino acids. S in food stuffs has been shown to be linked to colon rectal cancer. It is believed to destroy vitamin A and promote the oxidation of the conjugated double bonds, and is also known to destroy vitamin B1. It also promotes allergies and accelerates the onset of allergy attacks. S toxicity produced laminar cortical necrosis in the brain of cattle (polioencephalomalacia) as a result of the interference with cytochrome oxidases, the terminal enzymes of respiratory in mitochondria (Bekeand and Hironaka, 1991 and Gould, 2000). A number of studies indicate that increasing dietary S reduces the bioavailability of selenium (Se). Sulfate was added to pregnant ewe's diets that were low in Se, causing increase the incidence of white muscle disease in their lamb (Spears, 2003). The maximum tolerable dietary intake of S is not recorded.

The present study was done in Assiut governorate in 3 areas in relation to the location of the industrial zone of superphosphate factory in Manqabad to evaluate some metallic emissions. The 3 chosen areas as the factory present were represented in Ezbet Gouda, Manqabad village and Dayrut city, respectively. Information concerning heavy metals in cheese and butter are relatively incomplete. Therefore, this work was planned to investigate the levels of one of metallic contaminants as Cd and some essential elements as Cu and P and S in raw milk, kareish cheese and cooking butter, where these products were highly consumed and these elements are considered the most waste product emitted from superphosphate manufacture.

MATERIALS and METHODS

Collection of samples:

A total of 93 random samples of raw milk, kareish cheese and cooking butter were obtained from 3 different areas related to the superphosphate factory which is located in Manqabad village, Assiut governorate. Distribution and numbers of samples were presented in Table 1. The samples were collected in glass containers, which were thoroughly cleaned with HCl, distilled water, and dried. All glass and plastic wares were rinsed with HNO3 (25%) to avoid metal contamination.

Table 1: Number and distribution of the examined samples.

Area	Distance from the factory	Milk	Kareish cheese	Cooking butter
Ezbet Gouda	Next to	33	5	5
Manqabad village	About 1.5 km	7	7	7
Dayrut city	About 53 km	7	17	5
Total		47	29	17

Physical examination: All samples were examined physically for color and flavor (APHA, 1985).

Detection of elements:

5 gm of each milk, kareish cheese and cooking butter were taken. Samples were digested with concentrated nitric acid. Samples were brought to a constant volume. Determination of Cd and Cu were carried out according to Agemain *et al.* (1980) and Parker *et al.* (1968), respectively, using the Atomic Absorption Spectrophotometer (AAS), GBC Avanta 906, Australia. The absorption and concentration were recorded directly from the digital scale of AAS in ppm. P and S were determined by the Molybdovanadate Colorimetric method (Vogel, 1969).

Statistical analysis:

The obtained data were statistically analyzed according to Sendecor and Cochran (1974) using student's "t" test. The obtained values in this study were compared with the permissible acceptable limits where Cd is 0.007 mg/kgbw (FAO/WHO, 1989), and the normal level of Cu is 0.1 ppm by Harrison (1993), S is 300 ppm according to Wattiaux (2003) and P is 700 ppm according to DRI (1997).

RESULTS

Physical examination:

The physical examination (color and flavor) revealed that all the examined milk, kareish cheese and cooking butter samples were within the normal color and flavor.

Chemical examination:

Results of chemical analysis of milk, kareish cheese and cooking butter samples for Cd, Cu, P and S were outlined in Tables 2, 3 and 4.

Table 2: Mean levels of metals and essential elements in milk samples recovered from the studied areas (ppm).

Element	Ezbet Gouda	Manqabad village	Dayrut city	Limits	References
Cd	0.1±0.001*	0.09±0.002*ab	0.01±*a 0.001	0.007 g/kg/bw (PTWI)	FAO/WHO (1989)
Cu	0.44±0.02*	0.49±0.02*ab	0.17±0.01a	0.1 ppm (NL)	Harrison (1993)
P	1160.1±15.8*	1093.7±17.5*ab	656.9±7.8*a	700 ppm (ADI)	DRI (1997)
S	440.4±12.5*	322.5±15.6*ab	293.8±11.8a	300 ppm (NL)	Wattiaux (2003)

PTWI=provisional tolerable weekly intake, NL= Normal level, ADI =acceptable daily intake.
* Means significant differences at p< (0.05) between the permissible limits and the concentrations in different areas.
a means a significant difference at p< (0.05) between the concentrations in both Manqabad, Dayrut and in Ezbet Gouda.
b means a significant difference at p< (0.05) between that of Manqabad and Dayrut concentrations.

Table 3: Mean levels of metals and essential elements in kareish cheese samples recovered from the studied areas (ppm).

Element	Ezbet Gouda	Manqabad village	Dayrut city	Limits	References
Cd	0.5±0.001*	0.15±0.002*ab	0.000±0.0a	0.05 mg/kg (MLS)	Egyptian organization standardization (1993)
Cu	1.89±0.002*	1.49±0.003*a	0.41±0.002*a	0.1-0.3 mg/kg (MLS)	Egyptian organization standardization (1993)
P	3350.0±15.2*	3130.0±17.2*ab	2848.0±8.6*a	700 ppm (ADI)	DRI (1997)
S	405.4±5.5*	377.5±6.5*ab	309.2±6.8*a	300 ppm (NL)	Wattiaux (2003)

MLS= maximum permissible limits, ADI =acceptable daily intake, NL= Normal level.
* Means significant differences at p< (0.05) between the permissible limits and the concentrations in different areas.
a means a significant difference at p< (0.05) between the concentrations in both Manqabad, Dayrut and in Ezbet Gouda.
b means a significant difference at p< (0.05) between that of Manqabad and Dayrut concentrations.

Table 4: Mean levels of metals and essential elements in cooking butter samples recovered from the studied areas (ppm).

Element	Ezbet Gouda	Manqabad village	Dayrut city	Limits	References
Cd	1.2±0.003*	0.01±0.001*ab	0.000±0.00a	0.05 mg/kg (MLS)	Egyptian organization standardization (1993)
Cu	0.9±0.002*	0.41±0.003*ab	0.25±0.006a	0.1-0.3 mg/kg (MLS)	Egyptian organization standardization (1993)
P	1489.2±13.5*	1306.0±15.4*ab	1090.4±13.8*a	700 ppm (ADI)	DRI (1997)
S	420.8±11.4*	408.1±12.6*ab	302.0±10.9a	300 ppm (NL)	Wattiaux (2003)

MLS= maximum permissible limits, ADI= acceptable daily intake, NL= Normal level.
* Means significant differences at p< (0.05) between the permissible limits and the concentrations in different areas.
a means a significant difference at p< (0.05) between the concentrations in both Manqabad, Dayrut and in Ezbet Gouda.
b means a significant difference at p< (0.05) between that of Manqabad and Dayrut concentrations.

DISCUSSION

Attention has been focused on milk, as it is nearly almost the perfect single foodstuff especially for children. Lactating animals may be exposed to high quantities of toxic metals in the environment through air, water and ingestion of polluted feed (Carl, 1991). In areas of high concentration of metallic pollutants, contamination of food and water can lead to intoxication (Protasowicki, 1992).

The analytical results of Cd levels in the examined milk samples were 0.1, 0.09 and 0.01 ppm in Ezbet Gouda, Manqabad village and Dayrut city, respectively (Table 2). They revealed a significant increase than the recorded permissible limits (0.007 ppm) of FAO/WHO, (1989). Tork (1994) and Fayed (1997) recorded higher levels as 0.113 and 0.2 ppm in raw milk samples, respectively. On contrast, Dwivedi *et al.* (1997) recorded lower levels also Alanis and Castro (1992) recorded Cd level less than <0.01 ppm. Galal (1990 and 1993) reported the concentration of Cd at or below the limits of detection 0.002 mg/kg. Carl (1991) recorded the PTWI of Cd in milk was 0.005-0.05 mg/kg. EL-Prince and Sharkawy (1999) estimated Cd levels as 0.017 and 0.019 ppm in cow and buffalo's milk, respectively. IDF (1991) reported that 0.00002-0.0008 mg/kg is the normal range of Cd in milk.

It is obvious from Table 3 that Cd levels in the examined kareish cheese samples revealed a significant increase in Ezbet Gouda and Manqabad village but not significant in Dayrut city as 0.5, 0.15, 0.0 ppm, respectively. 0.05 mg/kg is MLS of Cd in processed cheese (Egyptian Organization Standardization, 1993). From the aforementioned results in Table 4, Cd levels in the examined cooking butter samples in Ezbet Gouda, Manqabad village and Dayrut city were 1.2, 0.01 and 0.0 ppm, respectively. FAO/WHO (1989) recommended that PTWI of Cd in food is 0.007 mg/kgbw. It considered PTWI for Cd of 0.0067-0.0083 mg/kg/bw/ week, applicable to adults as well as infants and children (Egyptian Organization Standardization, 1993).

Elevation of Cd concentration in milk from lactating animals could be attributed to the greater ingestion of contaminated feed and water and inhalation of fumes and dusts from the industrial activities (Dwivedi *et al.*, 1997).

The mean values of Cu concentrations in the examined milk samples obtained from Ezbet Gouda, Manqabad village and Dayrut city (Table 2), were 0.44, 0.49 and 0.17 ppm, respectively. These levels approximately equal the results obtained by Sharkawy and Hussein (2002). These values were higher than that intended by Favretto and Marletta (1984) and Ibrahim *et at.* (1984) as Cu levels were 0.136 and 0.132 ppm in cow and buffalo's milk, respectively, Shehata and Saad (1992) and Fayed (1997). EL-Malt (2001) found that Cu level in milk samples from different areas in Assiut governorate was 0.092, 0.029, 0.127 and 0.11 ppm.

The mean levels of Cu concentrations in the examined kareish cheese and cooking butter samples were 1.89 and 0.9 ppm in Ezbet

Gouda, 1.49 and 0.41 ppm in Manqabad village and 0.41 and 0.25 ppm in Dayrut city, respectively (Tables 3 and 4). These levels showed a significant increase than the normal recorded level. 0.1 and 0.3 mg/kg are the maximum Egyptian permissible limits of Cu in low fat cheese and processed cheese with plant oil, respectively (Egyptian organization Standardization, 1993). Ockerman (1978) reported that 0.09 mg/100g is the normal Cu level in hard cheese. 66.6% of local hard cheese and 40% of cheese samples contaminated with levels higher than 0.09 mg/100g dry weight for Cu. 100% of the imported and local processed cheese samples were found to contain more than 0.3 mg/kg.

The normal level of Cu in milk is not more than 0.3 ppm as reported by Underwood (1977) and Forstner and Prosi (1979) or less than 0.1 mg/kg as stated by Harrison (1993). Burch and Hahn (1983) had observed that milk and milk products are poor sources of Cu. A daily intake of 1.5-3.0 mg of Cu is recommended for adults, whereas in children the recommendation is 0.7-2.0 mg (FNB, 1989). The MAD load of Cu ranged from 50 to 500 Ug/kg/day (CAC, 1984).

The high level of Cu in examined milk and milk products samples may be due to the wide application of Cu in agriculture and industry, therefore, it is potentially very hazardous trace element and very toxic at higher concentrations.

The analytical results of P concentrations in the examined milk samples were 1160.1, 1093.7 and 656.9 ppm in Ezbet Gouda, Manqabad village and Dayrut city, respectively (Table 2). These values were significantly increased than the normal P content in milk. The mean levels of P in the examined kareish cheese and cooking butter samples were significantly increased than the normal content. These values were 3350.0 and 1489.2 ppm in Ezbet Gouda, 3130.0 and 1306.0 ppm in Manqabad village and 2848.0 and 1090.4 ppm in Dayrut city, respectively (Table 3 and 4).

The average concentrations of P in milk samples was 637.1 mg/L (Alanis and Castro, 1992). Recommended dietary allowance (RDA) of P is 700 ppm as recorded by DRI (1997). ADI of P set by FAO/WHO (1989) committee is fixed at 30 and 70 mg/kg/bw. In the light of the increasing application of phosphates in food industries, the question arises whether these permissible limits are not exceeded by certain population group (El-Shaarawy and Reith, 1979). High levels of P may be attributed to long application of phosphates, which used as fertilizer and as animal and feed supplements. They are also used the manufacture of industrial chemicals and pharmaceuticals and as detergent builders.

High phosphate concentrations in surface waters may indicate fertilizer runoff; domestic waste discharges (Sharpely *et al.*, 1994).

Levels of S in the examined milk samples showed a significant increase than normal level in Ezbet Gouda, Manqabad village but not significant in Dayrut city. These mean values were 440.4, 322.5 and 293.8 ppm, respectively (Table 2). Values of S revealed a significant increase in the examined kareish cheese and cooking butter samples, as 405.4 and 420.8 in Ezbet Gouda, 377.5 and 408.1 ppm in Manqabad village, respectively. S showed a significant increase in kareish cheese in Dayrut city as mean values as 309.2 ppm but not significant in cooking butter as 302.0 ppm (Table 3 and 4). The Babcock institute of dairy research recorded that the normal S content in milk is 300 ppm (Wattiaux, 2003). Excess ingestion of S from soil by lactating animals leads to increase S concentration in blood and consequently the milk is produced containing high S content (Spears, 2003).

The obtained results showed a significant increase in Cd, Cu, P and S levels than that previously recorded of MAL and also than the recorded normal levels. This increase in relation to the examined milk samples was very obvious and significant in Ezbet Gouda than was estimated in Manqabad village and Dayrut city. A significant increase than the limits also recoded in Manqabad village that sited near the factory and it considers the nearest village to the factory. This elevation was obtained also in the examined kareish cheese and cooking butter samples. The lowest concentrations of Cd, Cu, P and S were recorded in Dayrut city, which is far from the factory by 53 km. Geographical distribution of these findings suggested that the presence of superphosphate factory in this area may lead to contamination of food and water, as well as, they are consumed by lactating animals in the surrounding environment leading to metallic pollution of milk and milk products.

In any environmental zone of industrial plant, a monitoring system for heavy metals must applied to be ensuring that milk and milk products are safe for human consumption. Regular investigation of the levels of these contaminants in milk and milk products is very essential, where these products are highly consumed in Egypt.

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