LEVELS OF SOME HEAVY METAL RESIDUES IN MILK PRODUCT POWDERS

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ABSTRACT

A total of 60 samples (20 of each) of milk powder, milk casein and milk whey were collected from different supermarkets in Alexandria governorate to determine levels of cadmium (Cd), lead (Pb), mercury (Hg), copper (Cu) and iron (Fe)., respectively. Our results indicated that the highest mean concentrations of cadmium, lead and copper (0.07p.p.m, 0.100 p.p.m, 0.25 p.p.m) were found in milk powder., respectively., while the lowest levels of cadmium, lead (0.05p.p.m, 0.04 p.p.m., respectively) were in casein and the lowest levels of copper (0.07p.p.m.) were in whey., respectively. At the same time, mercury was not deteeted in any of the examined samples. Concerning iron, the highest level (3.94 p.p.m) was in milk casein. Results showed that milk powder and milk whey samples showed levels of eadmium above the Egyptian permissible limits (0.05 p.p.m) at the main time, all the samples had levels of pb, Cu and Fe within the Egyptian permissible limits (0.1p.p.m, 5 p.p.m and 20 p.p.m for Pb, Cu and Fe, respeetively).

INTRODUCTION

Milk is recognized as an almost complete food product in the human diet because it provides all macro nutrients (such as proteins, lipids and carbohydrates) and all micro nutrients (elements, vitamins, enzymes) **(Kira and Maio, 2004)**. Whey is one of the proteins found in milk (the other is casein). Whey protein accounts for only about 20% of the total protein found in milk, while casein makes up about 80% or milk protein. Long considered a useless by-product of dairy (cheese) manufacturing, it has a long history of use as a cheap protein source for low-cost protein powders and used to be viewed as a "disposal problem" for the dairy industry. Milk serum (whey) proteins are those which remain in solution at the pH of casein precipitation. **(Nupur, Goyal and Gandh, 2009)**.

Milk and milk products contain more than twenty different trace elements, most of them are essential and very important such as copper, zinc, manganese and iron. These metals are cofactors in many enzymes and play an important role in many physiological functions of man and animals. Lack of the metals causes disturbances and pathological conditions Environmental pollution with chemical residues such as heavy metals leads to growing interest in metal contamination in milk and milk products, **(Schutmacher., et al**

1991). The toxic metal content of milk, dairy products (Cd, Pb, Hg) is due to several factors, in particular environmental conditions, manufacturing processes **(Aniello-Anastasio; et al., 2006)**. Toxicity of metals is closely related to age, sex, rout of exposure, level of intake, solubility, metal oxidation state, retention percentage, duration of exposure frequency of intake, absorption rate and mechanisms/ efficiency of excretion **(Mertz., 1986)**. Pollution of the environment with metals such as lead is world wide problem. Lead alkyl additives in petrol are combusted and emitted into the atmosphere and can be responsible for high concentration of lead in some vegetation, road side, soil, air, water and plants. Lead is toxic to the blood and the nervous, urinary, gastric and genital systems. Furthermore, it is also implicates in causing carcinogenesis, mutagenesis and teratogenesis in experimental animals **(Baht and May 1997)**. On the other hand, cadmium is easly volatilized at the operating temp's of common industrial process, much of the Cd in the atmosphere results from incineration of ferrous scrap and metallurgy process. Cd is implicated in high blood pressure, prostate cancer, mutations and foetal (embryonic) death **(Thomas., et al., 1972)**.

Mercury is a toxic heavy metals, it may contaminate food from different sources like natural sources or man made sources. Natural sources include degassing of earth's crust, emission from volcanoes and evaporation form the natural bodies of water (**National Academy of Science, 1978**). The most important sources of man made mercury contamination of food is the mining activities, other important man made sources are the combustion of fossil fuels, the smelting of metal sulfide ores, the production of cement and refuse incineration. The major source of mercury causing local problems has been from chloralkali plants which use mercury as an electrode in cells for the manufacture of Cl2, also Hg is used in many industrial processes. Mercury cause damage to the central (nervous system) furthermore, it can be implicated with a development of autoimmunity such as rheumatoid arthritis, infertility and hypertension **(Anderson 2000)**. Therefore, the aim of this study was to determine the levels of some heavy metals in powder milk, casein, and whey and to discuss it's public health significance on human health.

MATERIALS AND METHODS

Sampling:

A total of 60 samples of milk powder , casein and whey (20 for each) were collected from Alexandria supermarkets. Samples were transferred in an isolated ice box to the laboratory and analyzed for heavy metals and iron.

Heavy metals analysis :

Cadmium (Cd), lead (Pb), copper (Cu) were determined in milk powder, casein and whey samples using atomic absorption spectrophotometer (Perkin Elmer 2380) after wet digestion of samples. They extracted from the acid leach with ammonium pyrrolidine dithiocarbamate methyl isobutyl ketone (APDC/MIBK) and the extracts were run on the flame atomic absorption spectrophotometer (**Richard and Rubinshapiro, 1986**). In case of Hg, the analysis was conducted according to **Honway and Danny (1985)**. Using flameless atomic absorption spectrophotometer.

Iron analysis :

It was determined in milk powder, casein and whey samples using flame atomic absorption spectrophotometer (Perkin Elmer 2380) according to Richard and Rubinshapiro, 1986.

RESULTS

Statistical analytical results of cadmium (Cd), lead (Pb), mercury (Hg), copper (Cu) and iron (Fe)., in milk powder, casein and whey are showed in Tables 1-2 and figures 1-4., respectively .

DISCUSSION

Trace elements may enter the milk during milk synthesis or by contamination after the milk is removed from the cow, for example from metal containers, etc. cows raised near industrial plants can have higher cadmium and Pb than those raised at a distance from such sources of these heavy metals. Cows raised near high ways can have higher Pb than those raised at a distance (**Enb. A., et al., 2009**).

Our results showed that the highest mean conc's of Cd, Pb, Cu (p.p.m) 0.019 p.p.m, 0.069 p.p.m 0.251 p.p.m was found in milk powder; respectively, while in case of mercury, it could not be deteeted in any of the examined samples. our results indicated that the mean conc's of Cd in milk powder and milk whey samples were above the Egyptian Standard (0.05 p.p.m), while levels of lead, copper in all the examined samples were within Egyptian Standard limits (0.1p.p.m., 5p.p.m, 20 p.p.m., respectively (EOS,1993, EOS., 2001) (Table 1 and Figures I, II, III).

It was found that the mean concentrations (ppb) of Cu, Cd, Pb in cow's milk samples available commercially in Saudi Arabia, were determined in 2 types of milk samples including fresh cow milk and liquid milk prepared from cow's milk powder. The mean concentrated values of Cu, Cd, Pb in fresh cow's milk were (48.9±0.6), (4.7±0.2), (3.5±0.2); respectively, those in cow's milk powder were (36.9±1.1), (3.1±0.3), (2.2±0.2); respectively., (Farid, S. M. et al., 2004).

It was found that the mean concentration of Pb in milk powder was ranged from 0.054 p.p.m. in milk powder to 1,100 mg/kg in Kasar cheese and from 0.009 p.p.m in milk whey powder to 1.051 p.p.m in Tulum cheese; respectively (**Ahmet Ayar., et al., 2008**).

It was indicated that lead and cadmium contents in commercial milks form China and Japan were studied. The levels of Cd, Pb in Chinese milk did not exceed the tolerance limits of Chinese national standards, and they were higher than those in Japanese commercial milks. (**Li-Qiang Qin, et al., 2009**).

Enb. A., et al., 2009, showed that Cd, Pb, Cu, mean concentrations in Buffalo's milk (mg/kg) were: 0.106 mg/kg, 0.062 mg/kg, and; 0.201 mg/kg ., respectively, at the same time, levels of Cd, Pb, Cu, in cow's milk were 0.068 mg/kg, 0.040 mg/kg, 0.131 mg/kg, and; respectively (**Enb. A., et al., 2009**).

It was found that the Cu contents of six brands of milk powder (mg/100gm) were 0.75 mg/100gm, 0.6, 1.02, 1.06, 1.51, 0.85 mg/100gm; respectively (**Akpanyung E. O., 2008**).

It was indicated that the mean mercury concentration of commercially available milk samples was 0.27±0.06 ng g-1 Hg (**Patricia Cava-Montesinos, et al., 2004**).

It was reported that the mean lead levels in the milk based infant formula, milk powder and condensed milk were 0.44±0.093, 0.23±0.038 and 0.12±0.013 p.p.m; respectively. The mean cadmium levels, were 0.031±0.005, 0.11±0.0217 and 0.032±0.005 p.p.m; respectively form milk based infant formula, milk powder and cadmium milk. The mean copper levels were 0.86±0.094, 0.21±0.024, 0.053±0.003 p.p.m. (**Aiad and Fayed., 2006**).

It was reported that levels of lead, cadmium in different brands of whole cream powdered milk samples was ranged from 0.2-0.3 p.p.m for lead and from 0.005 to 0.008 p.p.m for Cd; respectively. The mean concentrations of Pb, Cd is almost comparable in both milks (**Talat Zamir and Altaf Hussain., 2001**).

Table (2) and Figure (VI) showed the statistical analytical results of iron in milk powder, casein and whey samples collected from Alexandria governorate, Our results indicated that casein showed the highest mean conc. of Fe (3.936 p.p.m) while the lowest was found in whey (2.549 p.p.m), at the main time, all the examined samples had levels of iron within the Egyptian standards (20p.p.m.) (**EOS 1993, EOS 2001**).

Comparing our results with the accepted upper limits of iron, it was detected at levels higher than the proposed European maximum limit of 20 μg/kg (**European commission, 1997**).

It was reported that the Fe content (μg/g) of 5 brands of market cow's milk was 0.22 μg/g, 0.14, 0.16, 0.22, 0.35 μg/g; respectively, and the composite, cow milk was 0.27 μg/gm (**Hiromi Ounstin., et al., 1985**).

The mean concentrations of iron (Fe) in fresh milk samples from supermarkets in Jeddah city, were: 413.5±2.1 ppb, respectively. (Kinsara and Farid 2008).

It was found that the Fe, contents of six brands of milk powder (mg/100gm) were 9.94 mg/100gm, 9.02, 11.82, 10.39, 10.04, 10.74, mg/100gm; respectively (**Akpanyung E. O., 2006**).

CONCLUSION

In conclusion, the present study showed that levels of heavy metals (Cd, pb, Hg and Cu) and iron in milk powder, casein and whey samples were within the Egyptian Standard permissible limits except levels of cadmium in milk powder and milk whey samples were exceeded the limits. Hence, it is recommended that the technology and quality control for milk processing should be improved and environmental pollution should be controlled.

Table (1): Statistical analytical results of heavy metals in milk powder, casein and whey .

Heavy metals (p.p.m.)	Milk powder			Casein			Whey		
	Range	Mean ± SD	Median	Range	Mean ± SD	Median	Range	Mean ± SD	Median
Cadmium(Cd)	0.03 – 0.11	0.07 ± 0.04	0.09	0.04 – 0.05	0.05 ± 0.01	0.05	0.06 – 0.09	0.07 ± 0.01	0.07
Lead (pb)	0.00 – 0.14	0.10 ± 0.06	0.12	0.01 – 0.08	0.06 ± 0.03	0.07	0.00 – 0.05	0.04 ± 0.02	0.04
Mercury (Hg)	ND			ND			ND		
Copper (Cu)	0.22 – 0.27	0.25* ± 0.02	0.25	0.07 – 0.10	0.09* ± 0.01	0.08	0.0 5 – 0.10	0.07 * ± 0.02	0.07

* : Statistically significant at $p \leq 0.05$

Table (2): Statistical analytical results of iron in milk powder, casein and whey .

Samples	Statistical analysis of iron		
	Range	**Mean ± SD**	**Median**
ilk powder	1.51 – 3.81	2.73 ± 1.04	2.95
Casein	2.26 – 5.81	3.94 ± 1.41	3.46
Whey	1.04 – 4.12	2.55 ± 1.32	2.64

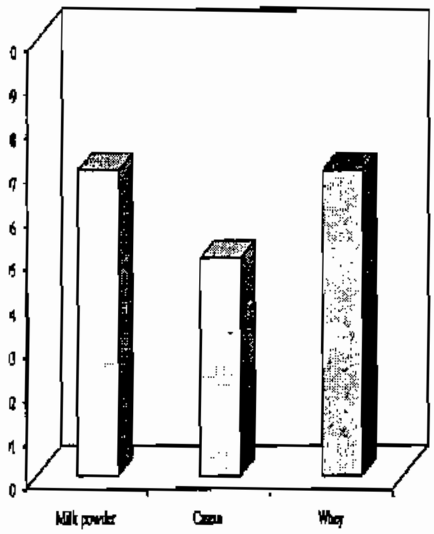

Figure (I): Levels of cadmium (Cd) p.p.m) in milk powder, casein, whey

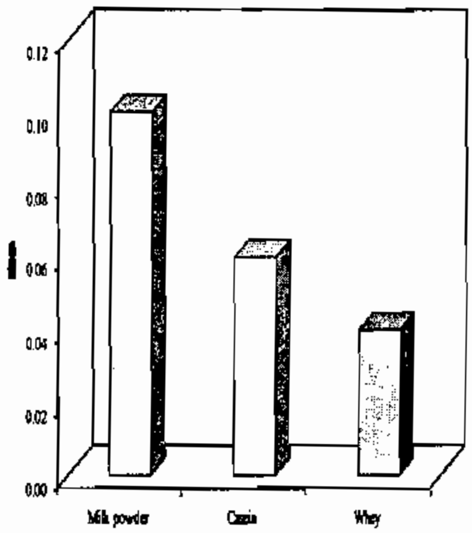

Figure (II): Levels of Lead (Pb) (p.p.m) in milk powder, casein, whey

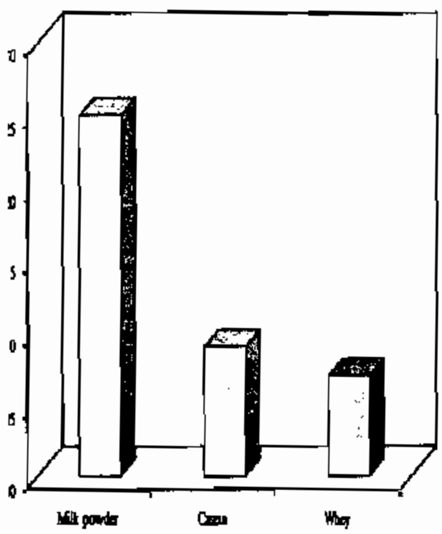

Figure (III): Levels of Copper (Cu) p.p.m) in milk powder, casein, whey

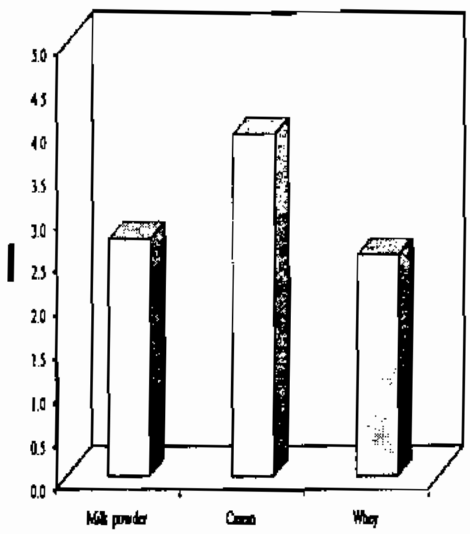

Figure (VI): Levels of Iron (Fe) (p.p.m) in milk powder, casein, whey

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الملخص العربى

تقديـــر مســتويات المعــادن الثقيلــة فى منتجــات اللـبن البــودرة

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لقد تم تقدير تركيزات الكادميوم والرصاص والزئبق والنحاس والحديد فى بعض منتجات اللبن البودرة مثل بودرة اللبن الجاف وبروتين اللبن ومصل الزئبق (الشرش) على التوالى وقد لوحظ أن متوسطات التركيزات كالآتى : فى حالة الكادميوم والرصاص والنحاس وجد أن :

أعلى تركيزات كانت فى اللبن البردرة (0.07، 0.100، 0.25 جزء فى المليون) على التوالى بينما كانت أقل تركيزات للكادميوم فى بروتين اللبن (0.05 جزء فى المليون) على التوالى بينما كان أقل تركيزات للرصاص والنحاس فى شرش اللبن (0.07،0.04 جزء فى المليون) وفى نفس الوقت كان الزئبق غير متواجد فى أى من العينات موضع الدراسة.

وفى حالة الحديد كان أعلى تركيز له فى بروتين اللبن بمتوسط تركيز 3.94 جزء فى المليون وكان أقل تركيز للحديد فى شرش اللبن بمتوسط تركيز 2.55 جزء فى المليون، كما أوضحت الدراسة أن جميع العينات موضع الدراسة كان متوسطات تركيزات المعادن بها فى الحدود المسموح بها (0.4، 0.3،0.05 للكادميوم والرصاص والنحاس على التوالى) فيما عد الزئبق فلم يتواجد فى أى من العينات موضع الدراسة وكذلك الكادميوم كان متوسط تركيزاته تتخطى الحدود المسموح بها فى اللبن البردرة وفى شرش اللبن.