

ESTIMATION OF SOME HEAVY METALS IN COW'S MILK IN ZAGAZIG CITY

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ABSTRACT

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This study estimated the residues of some heavy metals of toxicological concern in milk. One hundred and fifty samples from dairy farm, market raw milk and vendors milk were collected from Zagazig City. Collected samples were examined for presence of lead (Pb), cadmium (Cd), mercury (Hg) copper (Cu) and Zinc (Zn) by using atomic absorption spectrometry. The mean concentrations were 0.716, 2.001, 2.11 for Pb; 0.871, 3.39, 4.11 for Cd; 0.911, 5.79, 6.37 for Hg; 2.81, 7.21, 7.72 for zinc and 2.111, 4.44, 4.45 (ng/L) for copper in farms, markets and vendors milk samples, respectively. The percentages of significant dairy farms, market milk and vendor samples exceeded the maximum permissible limits were 30, 44 and 52% for lead, 26, 100 and 100% for cadmium, 12, 22 and 28% for mercury, 22, 26 and 32% for zinc, 50, 90 and 96% for copper. The statistical analysis regarding the data obtained from farms, markets and vendors milk revealed a low moderate and high significant differences in lead, copper, cadmium, mercury and zinc respectively. The public health and suggest precaution to minimize the level of such heavy metals in milk were discussed.

Key words: *Heavy metals, Cows milk, Public health*

INTRODUCTION

Inorganic or aggregated forms of chemical substances (metalloids, heavy metals etc..) in feed and food represent a severe risk for their long term toxicological effects. Heavy metals are widely dispersed in the environment. The toxicity induced by excessive levels of some of these elements such as cadmium (Cd), lead (Pb), Zinc (Zn) and mercury (Hg) are well known (Kabzinski, 1998).

The toxic metal content of milk and dairy products is due to several factors in particular environmental conditions, the manufacturing process and the possible contamination during several steps of the manufacturing processes (Caggiano *et al.*, 2005).

Milk contain most of the nutrients necessary for healthy food and in some groups such as children elderly, it may constitute the main food or even the only one (Lawrance and Friedman 1995 and Tripathi *et al.*, 1999).

Heavy metal residues are highly toxic but many of them (e.g. copper and zinc) are essential activators for certain enzymes, vitamin and hormones, only at low concentrations. They are able to accumulate in the living tissues and organs leading to toxicity in man and animals. It is important to distinguish between their hazard effect and nutritional requirements (Garcia *et al.*, 1999; Saad *et al.*, 2001 and Llobet *et al.*, 2003).

Heavy metals of toxicological concern are lead (Pb), cadmium (Cd), mercury (Hg), copper (Cu) and Zinc (Kabzinski, 1998). They are widely distributed in air, agricultural lands, water, effluents from heavy industries, drainage, fertilizers, sludge applied in the fields and stainless steel used in dairy equipment (USEPA, 1993; Miner *et al.*, 1997 and Naresh *et al.*, 1999).

Copper, lead and cadmium are often deposited in lakes and streams from the air and considered as main source of water pollution that may be utilized by dairy animals or used for washing dairy utensils (Vesiland *et al.*, 1990; Walker, 1999 and Enb *et al.*, 2009).

In recent years, much attention has been paid to the possible danger of metal poisoning in human. It has been reported that lead, cadmium, zinc, copper and mercury are concentrated mostly in the kidney and liver leading to kidney damage and liver cirrhosis (Coggiano *et al.*, 2005). They constitute severe threat to human health due to their cumulative nature resulting in cancer, renal failure, human hypertension, neuropathy of both central and peripheral nervous system, gastroenteritis, diabetes mellitus, anemia and ostiomalacia (Klopov, 1998; Eife *et al.*, 1999 and Hagag and Fayz, 2012).

Because of the high risk associated with the consumption of milk with such toxic pollutants, the aim of the present study was to: determine the

concentration of Cd, Pb, Cu, Zn and Hg in farm, marked raw milk samples and vendors milk to set alarm for the public about their hazard effects.

MATERIALS and METHODS

The samples were collected in 8 areas places from Zagazig City with different pollution impact (high volume of traffic, industrial plants, dumps, waste-incinerators, metropolitan areas, small-medium towns, intensive agricultural activities).

Collection of samples:

A total of one hundred and fifty samples were collected from of dairy farms cow's milk, market raw milk and vendors (fifty of each), from 8 areas in Sharkia Governorate with different pollution impact (high volume of traffic industrial plants, dumpo, waste incinators, metro polition areas, small medium towns, intensive agricultural activities). The collected samples were aseptically collected and transferred to the laboratory to be examined for heavy metal residues.

Market raw milk samples were subjected to peroxidase test to exclude all samples proved to be heat treated according to Mendil, (2006).

Preparation of samples:

All samples were prepared according to FDA, (1993). Each milk sample was lyophilized and transferred into decontaminated polyethylene containers. The samples were then dried in an oven at 102°C for 6 hrs

to remove the trace of moisture. Slow charring was carried out on hot plate followed by calcination at 400°C for 6 hrs in muffle furnace until white ash production. The ash was dissolved in one ml of nitric acid and made up to 25 ml with double distilled water.

Extraction of heavy metal according to Lameiras *et al.* (1998):

Milk samples were extracted by adding 4ml of the prepared sample into polyethylene bottle with 10ml suspension solution composed of 0.5g ammonium dihydrogen phosphate, 20ml ethanol, 50ml concentrated hydrogen peroxide and one ml concentrated nitric acid to 100ml deionized water. The mixture was mixed and filtered through 0.45µm membrane filter.

Determination of heavy metals:

Twenty microlitre of the filtrate were injected into the furnace (HCA-400°C ± 10) and run for 6 hrs until correlated peaks areas were obtained. Calibration was performed with aqueous standards prepared with the same suspension solution. Heavy metals were estimated using electrothermal atomic absorption spectrophotometer (ETAAS). Detection limits were calculated corresponding to three times of the standards. Accuracy was checked with recovery assays by adding known amount of standards to five different randomly samples and processing the mixtures as described for experimental samples according to Kabzinski, (1998) and Lameiras *et al.* (1998).

RESULTS

Table 1: Levels of heavy metals (ng/L) in dairy farm milk (cow's milk)

Type	Minimum	Maximum	Mean
Lead [*]	0.004	1.024	0.716 ± 0.025
Cadmium ^{**}	0.009	2.251	0.871 ± 0.035
Mercury ^{***}	0.003	1.113	0.911 ± 0.003
Zinc ^{***}	0.008	3.987	2.810 ± 0.011
Copper [*]	0.022	3.798	2.111 ± 0.014

*Significant (P ≥ 0.05)

**Significant (P ≥ 0.01)

***Significant (P ≥ 0.001)

Table 2: Levels of heavy metals (ng/L) in market raw milk samples

Type	Minimum	Maximum	Mean
Lead [*]	0.018	3.150	2.001 ± 0.01
Cadmium ^{**}	0.030	5.680	3.390 ± 0.32
Mercury ^{***}	0.050	9.450	5.790 ± 0.12
Zinc ^{***}	1.744	11.05	7.210 ± 0.24
Copper [*]	0.310	6.410	4.440 ± 0.12

*Significant (P ≥ 0.05)

**Significant (P ≥ 0.01)

***Significant (P ≥ 0.001)

Table 3: Levels of heavy metals (ng/L) in vendor milk samples

Type	Minimum	Maximum	Mean
Lead*	0.019	3.260	2.113 ± 0.02
Cadmium**	0.031	5.811	4.119 ± 0.51
Mercury***	0.061	10.240	6.371 ± 0.12
Zinc***	1.788	11.02	7.721 ± 0.22
Copper*	0.219	6.884	4.450 ± 0.12

*Significant (P ≥ 0.05)

**Significant (P ≥ 0.01)

***Significant (P ≥ 0.001)

Table 4: The number of milk samples exceeded the maximum permissible limits

Heavy metals	Limits (ng/L)	Farm milk		Market raw milk		Vender milk	
		No.	%	No.	%	No.	%
Lead	0.05	15	30	22	44	26	52
Cadmium	0.02	13	26	50	100	50	100
Mercury	4.0	6	12	11	22	14	28
Zinc	3.0	11	22	13	26	16	32
Copper	0.3	25	50	45	90	48	96

DISCUSSION

The percentages of the examined farm, market raw milk and vendors milk samples that exceeded the maximum permissible limits were in Table (4) 30, 44 and 52 for lead, 26, 100 and 100 for cadmium; 12, 22 and 28 for mercury; 22, 26 and 32 for zinc; 50, 90 and 96 copper. Nearly similar findings were reported by Saad *et al.* (2001).

The percentages of heavy above MRL in dairy farm milk may be attributed to agriculture practices, plants and fertilizers that remain in the feed consumed by dairy animals. This may lead to bioaccumulation of these metals in animal's tissues resulting in production of milk with high metal residues (Gengelbach and Spears, 1998 and Kodrik *et al.*, 2011).

The most probable explanation for the high level of heavy metals in raw market milk may occur during milk transportation specially in polluted air, bad storage, contact with equipment employed as mechanical milkers, cadmium plated containers and tanker lorries. The transferred metals from equipment may exceed those originally present in the dairy farm milk (Coni *et al.*, 1999 and Hagag and Fayz, 2012).

From the obtained results, it was clear from Tables (1, 2 and 3) that the mean value of lead, cadmium, mercury, zinc and copper concentration in dairy farm milk, raw market milk and vendor milk were 0.716 ±

0.025, 2.001 ± 0.01, 2.113 ± 0.02, 0.871 ± 0.035, 3.390 ± 0.32, 4.11 ± 0.51, 0.911 ± 0.003, 5.790 ± 0.12, 6.371 ± 0.12, 2.81 ± 0.011, 7.210 ± 0.24, 7.721 ± 0.22 and 2.111 ± 0.014, 4.44 ± 1.2, 4.450 ± 0.12 ng/L, respectively.

Difference in cadmium (P>0.01) and high significant difference in mercury and zinc (P>0.01) were observed, respectively (Tables 1 and 2). The significant difference in Cd, Zn and Hg nearly similar to the findings reported by Kirova (1995). Lower quantities were recorded by Carl, (1991) and Enas and Sharkawy, (1999).

On the other side, these high levels were reported by Fathi *et al.* (1997) and Naresh *et al.* (1999). This variation was probably attributed to the use of different analytical procedures.

The obtained results declared that the concentration of heavy metals in market raw milk samples considerably higher than those detected in dairy farm milk. This may be due to the different sources of samples which depend on the surrounding circumstances (Saad *et al.*, 2001 and Kodrik *et al.*, 2011).

According to the maximum permissible limits (MPL) of human daily intake recorded, continuous consumption of milk with such pollutants may lead to chronic toxicity including nervous system damage, mental retardation, kidney dysfunction, nausea, sever colic, diarrhea, persistent restlessness and long lasting

rashes (Walker, 1999). Consumption of such milk particularly from polluted environment may pose human health hazards (Annon, 1996 and Zatterstrom, 1999).

CONCLUSION

To safe guard human health, a number of factors are to be into consideration for controlling heavy metal residues in milk starting from crop production by application good manufacturing practice, personal training and minimizing use of sludge for land fertilization, periodical monitoring of heavy metals in different types of milk.

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قياس بعض المعادن الثقيلة في لبن البقر في مدينة الزقازيق

أحمد عبد الخالق ، عزة جودة مصيلحي ، منى طلعت رسلان

تم في هذه الدراسة تحديد بقايا المعادن الثقيلة في الألبان، فقد تم تجميع ١٥٠ عينة من ألبان المزارع والأسواق والباعة الجائلين من أماكن متفرقة في مدينة الزقازيق. تم فحص هذه العينات لقياس تواجد بقايا بعض المعادن الثقيلة مثل الرصاص والكاديوم والزنك والنحاس والزنك باستخدام طريقة الامتصاص الذري مقدراً بـ ng/L، وكانت متوسطات التركيزات الموجودة بالنانوجرام لكل لتر هي ٠.٧١٦، ٢.٠٠١، ٢.١١ للرصاص و ٠.٨٧١، ٣.٣٩، ٤.١١ للكاديوم و ٠.٩١١، ٥.٧٩، ٦.٣٧ للزنك و ٢.٨١، ٧.٢١، ٧.٧٢ للنحاس و ٢.١١١، ٤.٤٤، ٤.٤٥ للنحاس علي التوالي في ألبان المزارع والسوبر ماركت والباعة الجائلين. وكانت نسبة العينات التي تزيد تركيزات المعادن الثقيلة عن النسبة المسموح بها عالمياً وهي (٣٠ و ٤٤ و ٥٢%) للرصاص، (٢٦ و ١٠٠ و ١٠٠%) للكاديوم، (١٢ و ٢٢ و ٢٨%) للزنك، (٢٢ و ٢٦ و ٣٢%) للزنك، (٥٠ و ٩٠ و ٩٦%) للنحاس. وبالتحليل الإحصائي لوحظ وجود تباين من الأقل إلي الأعلى في الرصاص والنحاس والكاديوم والزنك في ألبان المزارع والسوبر ماركت والباعة الجائلين. وقد تمت مناقشة الآثار الصحية لكل المعادن والطرق المناسبة لتقليل مستوي بقايا هذه المعادن الثقيلة في الألبان وذلك حرصاً علي الصحة العامة للإنسان لمستهلكي هذه اللبن ومنتجاتها.