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ESTIMATION OF SOME HEAVY METALS CONCENTRATION IN WATER SUPPLY OF DAIRY FARM AND RAW COW'S MILK SOLD IN ASSIUT CITY, EGYPT

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ABSTRACT

A total of 120 random samples of dairy water supply, raw cow's milk from different, dairy farms, dairy shops and street vendors (30 samples each) Assiut, Egypt during the period from April 2018 to march 2019 to estimate concentration of Lead, cadmium, manganese and Mercury in water supply of dairy farm and dairy farms, dairy shops and street vendors raw milk samples in Assiut governorate, Egypt. Statistical analytical results of heavy metals mean values (ppm) in dairy farm water supply were 0.192± 0.006, 0.0005± 0.0001, 0.950± 0.0034 and 0.648± 0.002 respectively. While in in dairy farm cow's milk they were 0.084± 0.026, 0.032± 0.067, 0.830± 0.002 and 3.523± 0.002 (ppm) respectively. But in in dairy shop cow's milk were with means 0.217± 0.045, 0.053± 0.067, 0.900± 0.002 and 4.200± 0.038, respectively. The street vendors cow's milk the mean values were found to be 0.289± 0.067, 0.064± 0.045, 0.954± 0.056 and 4.769± 0.052 respectively. All results of heavy metals were in concentration higher than Maximum permissible limits. The health importance of heavy metals and methods of control are discussed.

***Key words*:** heavy metals, water supply, dairy farm, raw cow's milk, Assiut, Egypt.

INTRODUCTION

Milk considered as one of the most important natural food for human at all stages of life. So a greater deal of efforts have been made to produce clean milk and milk products to become save for use and protect it from pollution by many materials as heavy metals. The most important widely distributed heavy metals of toxicological concern are lead (Pb), cadmium (Cd), mercury (Hg) and manganese (Kabzinski, 1998). They are widely distributed in air, water from heavy industries, drainage, fertilizers, sludge applied in the fields and stainless steel used in diary equipment (Naresh *et al.,* 1999). They also may be a pollutant from the use of agricultural pesticides and related chemicals, unhygienic weed out wastes and diffusion of sewage quagmire (Tona *et al.*, 2013). Also, they often deposited in lakes and streams from the air and considered as a main source of water pollution that may be utilized by dairy animals (Enb *et al.,* 2009).

Drinking of polluted water by toxic heavy metals have been responsible for health problems in dairy farms (Mohod and Dhote, 2013). However, water used in the dairy farms for drinking of livestock may be transmitted to dairy animals and appear in a high level in their milk.

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Milk polluted with heavy metals is considered a vehicle for transmission of illness among consumers, especially in developing countries where food hygiene is still under-way due to lack of food hygienists, modern diagnostic methods, beside some environmental conditions and financial difficulties (ELAtrash and Atoweir, 2014). They are able to accumulate in the living tissues and organs as kidney and liver leading to kidney damage and liver cirrhosis (Coggiano *et al.*, 2005) and may be cause toxicity in man and animals 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 (Malhat *et al.,* 2012).

This work was planned to estimate concentration of Lead, cadmium ,manganese and Mercury in water supply of dairy farm and dairy farms, dairy shops and street vendors raw milk samples sold in Assiut governorate, Egypt.

MATERIALS AND METHODS

Collection and handling of the samples:
A total of 120 random samples of dairy water supply, raw cow's milk from different, dairy farms and dairy shops and street vendors (30 samples each) Assiut, Egypt during the period from April 2018 to march 2019 were collected in a clean, dry and sterile containers, and transferred to the laboratory with a

minimum of delay, whereas they directly examined or held in the refrigerator until time of examination.

***Preparation, digestion* and estimation of samples:**

Water digestion (Chau *et al.*, 1979):
Five milliliter of each sample was transferred to a digestion flask where it was treated with 5 ml of nitric and perchloric acids mixture (HNO3: HCLO4 = 4:1 v/v). The samples were left to be stand for the cold digestion overnight, and then were heated on a hot plate (model 1030-RuMO 100) at 70˚C till disappearance of the brown fumes of NO3 and the sample become clear. After cooling, each sample was diluted to 25 ml with bi-distilled water and filtered through ashless filter paper (Whatman paper). The digested samples were kept refrigerated in 50 ml propylene bottles till analysis.

Milk digestion (Slavin *et al.*, 1975):
Milk samples were digesed according to Slavin *et al.* (1975) with some modification as follow:

From each milk sample, 25 ml was drawn with clean sterile 25 ml glass pipette and placed in clean dried 250 ml Erlenmeyer flask.

Erlenmeyer flasks that contained milk samples were put in hot air oven at 100C for half an hour and then were left at 50C for 24 hours till evaporation of water from the milk sample occurred .

25 ml digestion mixture (Equal volumes of concentrated nitric acid and 72% perchloric acid) were added to each flask, shaked and the acid was allowed to react at room temperature for 24 hours to facilitate the processes of digestion.

After this the flasks were put on hot plate at approximately 100C, shaked and several milliliters of concentrated nitric acid were added in each flask during the process of heating. Heating continued till the sample become colorless (complete digestion of the sample and disappearance of the brown gas (Nitricoxide, NO3) after its evaporation from the flask).

Samples were allowed to cool, filtered with filter paper, flasks then washed out several times with ion free water till the final volume of the digested sample reach 25 ml. These samples stored at refrigerator tell their analysis and estimation of Aluminum.

Determination of Lead, Cadmium, Manganese and Mercury in milk samples in ppm were estimated in the digested milk samples by means of, atomic absorption spectrophotometer (Shimadzu Atomic absorption / flame spectrophotometer ModelAA630-02P / N204-27600-02AA630-02), Kyoto-Japan. Analysis line wave length, Lamp current, slite width, Brner flam and support gas flow (e /min) for it were Analysis linewave length: nm, Lamp crrent: mA, Slit width: Burner flam: cm air-C2H2, Spport gas flow (e /min.)

RESULTS

Table 1: Statistical analytical results of heavy metals concentration (ppm) in dairy farm water supply.

Heavy metals	*No. of exam. samples*	*Positive samples*					**Maximum *permissible limits* according to WHO, 2011 (ppm)**
		No.	***%***	**Minimum**	**Maximum**	**Mean ± SE**	
Lead	30	22	73.33	0.156	0.235	0.192± 0.006	0.01
Cadmium	30	17	56.66	0.0004	0.0007	0.0005± 0.0001	0.003
Manganese	30	12	40	0.460	1.380	0.950± 0.0034	0.1
Mercury	30	7	23.33	0.002	0.780	0.648± 0.002	0.5

Table 2: *Statistical analytical results* of heavy metals concentration (ppm) in dairy farm cow's milk *samples.*

Heavy metals	*No.of exam.samples*	*Positive samples*				
		No.	***%***	**Minimum**	**Maximum**	**Mean ± SE**
Lead	30	19	63.33	0.019	0.212	0.084± 0.026
Cadmium	30	11	36.66	0.003	0.038	0.032± 0.067
Manganese	30	8	26.66	0.40	1.300	0.830± 0.002
Mercury	*30*	*5*	*16.66*	*0.001*	*5.400*	*3.523*± 0.002

Table 3: *Statistical analytical results* of heavy metals concentration (ppm) in dairy shop milk in raw cow's milk *samples.*

Heavy metals	***No. of exam. samples***	***Positive samples***				
		No.	***%***	**Minimum**	**Maximum**	**Mean ± SE**
Lead	30	22	73.33	0.082	0.496	0.217± 0.045
Cadmium	30	14	46.66	0.008	0.085	0.053± 0.067
Manganese	30	8	26.66	0.540	1.380	0.900± 0.002
Mercury	30	6	30	0. 012	5.200	4.200± 0.038

Table 4: *Statistical analytical results* of heavy metals concentration (ppm) in street vendors milk in raw cow's milk *samples.*

Heavy metals	***No. of exam. samples***	***Positive samples***				
		No.	***%***	**Minimum**	**Maximum**	**Mean ± SE**
Lead	30	23	76.66	0.089	0.568	0.289± 0.067
Cadmium	30	16	53.33	0.006	0.096	0.064± 0.045
Manganese	30	8	26.66	0.630	1.700	0.954± 0.056
Mercury	30	8	20	0.018	5.986	4.769± 0.052

Table 5: The relationship between international permissible limits of heavy metals (ppm) and mean finding in dairy farm water supply, dairy farm's, dairy shop's and street vendor 's cow's milk.

heavy metals	**Mean ± SE dairy shop**	**Mean ± SE street vendors**	**Mean ± SE dairy farm**	**Maximum *permissible limits* According to IDF Standard (1979) and Codex (2007)**
Lead	0.084± 0.026	0.217± 0.045	0.289± 0.067	0.02
Cadmium	0.032± 0.067	0.053± 0.067	0.064± 0.045	0.0026
Manganese	0.830± 0.002	0.900± 0.002	0.954± 0.056	0.05
Mercury	3.523± 0.002	4.200± 0.038	4.769± 0.052	4.0

DISCUSSION

Polluted drinking water play important roles in transmition of many types of heavy metals to dairy animals and appear in milk causing many problems to the consumers for man and animals may reach to a toxicity level (Jaleel *et al.,* 2001). Lead (Pb), cadmium (Cd), manganese (Mn) and mercury (Hg) are the most distributed heavy metals in water (Kabzinski, 1998).

The summarized results in Tables 1 showed that Statistical analytical results of heavy metals (ppm) in dairy farm water supply were 22(73.33%), 17 (56.66%), 12(40 %) and 7(23.33 %) of examined samples (30 samples) + ve for Lead, Cadmium, Manganese and Mercury, respectively. The incidence of lead, cadmium, manganese and mercury (ppm) ranged from 0.156, 0.0004, 0.460 and 0.002 to 0.235, 0.0007, 1.380 and 0.780 with mean ranges 0.192± 0.006, 0.0005± 0.073, 0.950± 0.0034 and 0.648± 0.002, respectively. In the other hand, these results of water samples were significantly higher in lead, Manganese and Mercury than Maximum permissible limits according to WHO, 2011 (ppm) but cadmium appear in save percentage which low the Maximum permissible *limits* according to WHO, 2011 (ppm) .

These results agree with that obtained by Jaleel *et al.* (2001), Nassef *et al.* (2006); Abdl-khalik *et al.* (2013); Wongsasuluk *et al.* (2014); Boateng *et al.* (2015); Aamer *et al.* (2016).

The obtained result in Table 2 revealed that *Statistical analytical results* of heavy metals (ppm) in dairy farm cow's milk were19 (63.33), 11 (36.66), 8 (26.66) and 5 (16.66) of examined samples + ve for Lead, Cadmium, Manganese and Mercury, respectively. The incidence of lead, cadmium, manganese and mercury (ppm) ranged from 0.019, 0.003, 0.40 and 0.001 to 0.212, 0.038, 1.300 and 5.400 with mean ranges 0.084± 0.026, 0.032± 0.067, 0.830± 0.002 and 3.523± 0.002 respectively.

The summarized results in Table 3 Pointed out *Statistical analytical results* of heavy metals (ppm) in dairy shop cow's milk were 22 (73.33), 14 (46.66), 8 (26.66) and 6 (30) of examined samples (30 samples) + ve for Lead, Cadmium, Manganese and Mercury respectively. And the incidence of lead, cadmium, manganese and mercury (ppm) ranged from 0.082, 0.008, 0.540 and 0.012 to, 0.496, 0.085, 1.380 and 5.200 with mean ranges 0.217± 0.045, 0.053± 0.067, 0.900± 0.002 and 4.200± 0.038, respectively.

The results of Table 4 revealed that *Statistical analytical results* of heavy metals (ppm) in street vendors cow's milk were 23 (76.66), 16(53.33), 8 (26.66) and 8 (26.66) of examined samples (30 samples) + ve for Lead, Cadmium, Manganese and Mercury respectively. And the incidence of lead, cadmium, manganese and mercury (ppm) were ranged from, 0.089, 0.006, 0.630 and 0.018 to 0.568, 0.096, 1.700 and 5.986 with a mean range 0.289± 0.067, 0.064± 0.045, 0.954± 0.056 and 4.769± 0.052 respectively.

Nearly similar results of lead, Cadmium and Mercury were obtained by Saad *et al.* (2001); Pavlovic *et al.* (2004); Gabryszuk *et al.* (2010); Bilandžić *et al.* (2011); Malhat *et al.* (2012); Abdl-khalik *et al.* (2013); Aamer *et al.* (2016). Same results were obtained by Haldar *et al.* (2003); Santos *et al.* (2015) for Manganese who found Mn in cow's milk with the range of 1.60 to 1.69 ppm.

The obtained results Table 5 mentioned that the mean finding of heavy metals in dairy farms, dairy shops and street vendor's cow's milk were significantly higher level of lead, Cadmium ,Manganese and Mercury than the maximum permissible *a*ccording to IDF Standard (1979) and Codex (2007).

Drinking water supply contain heavy metals concentration higher than Maximum permissible limits according to WHO, (2011) (ppm) mean level of this may be due to contamination from air, water from heavy industries, drainage, fertilizers, sludge applied in the fields and stainless steel used in diary equipment (Naresh *et al.,* 1999). Dairy farm milk contain heavy metals in concentration higher than maximum permissible limits according to IDF Standard (1979) and Codex (2007) where 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; Kodrik *et al.,* 2011).

Polluted Milk with heavy metals is considered a vehicle for transmission of illness among consumers, which accumulate in the living tissues and organs as kidney and liver leading to kidney damage and liver cirrhosis (Coggiano *et al.,* 2005). Resulting in cancer, renal failure, human hypertension, neuropathy of both central and peripheral nervous system, gastroenteritis, diabetes mellitus, anemia and ostiomalacia (Hagag and Fayz, 2012). And may be cause toxicity in man and animals. (Klopov, 1998 and Eife *et al.,* 1999).

CONCLUSION

At the end of this study we can conclude that Polluted drinking water play important roles in transition of many types of heavy metals as Lead, cadmium, manganese and mercury to dairy animals and appear in milk causing many problems (Jaleel *et al.,* 2001) and there is a significant relationship between heavy metal pollution of milk and those in water samples. This mean that the main source of milk polluted with heavy metals from water contamination.

Water supply must be protected from chemical contaminants, effluents and sewage to assure health safety for human and animals.

Periodical examination of milk for chemical pollution specially heavy metals.

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تقدير تركيز بعض المعادن الثقيلة في مصادرالمياه فى مزارع الألبان وحليب البقر الخام المباع في مدينة أسيوط ، مصر

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تم جمع ١٢٠ عينة عشوائية من مصادر المياه فى مزارع الألبان وحليب البقر الخام من مختلف مزارع الألبان ومحلات الألبان والباعة المتجولين (٣٠ عينة لكل منهما) في محافظة أسيوط خلال الفترة من أبريل ٢٠١٨ إلى مارس ٢٠١٩ لتقدير تركيز الرصاص والكادميوم والمنجنيز والزئبق وكانت النتائج التحليلية والإحصائية للمعادن الثقيلة (ppm) في مصادر مياه مزارع الألبان بمتوسط ٠,٠٠٦ ± ٠,١٩٢ و ٠,٠٠٠١ ± ٠,٠٠٠٥ و ٠,٠٠٣٤ ± ٠,٩٥٠ و ٠,٠٠٢ ± ٠,٦٤٨ جزء فى المليون على التوالي. في حين في لبن مزارع الألبان كانت بمتوسط ٠,٠٢٦ ± ٠,٠٨٤ و ٠,٠٦٧ ± ٠,٠٣٢ و ٠,٠٠٢ ± ٠,٨٣٠و٠,٠٠٢ ± ٣,٥٢٣ على التوالي . ولكن في محلات الألبان ، كان حليب الأبقار يتراوح في المتوسط ٠,٠٤٥ ± ٠,٢١٧ و ٠,٠٦٧ ± ٠,٠٥٣ و٠,٠٠٢ ± ٠,٩٠٠ و٠,٠٣٨ ± ٤,٢٠٠ على التوالي ولكن في الباعة المتجولين كانوا حليب البقر ٠,٠٦٧ ± ٠,٢٩٨ و ٠,٠٤٥ ± ٠,٠٦٤ و٠,٠٥٦ ± ٠,٩٥٤ و٠,٠٥٢ ± ٤,٧٦٩ على التوالى .

وكانت جميع نتائج المعادن الثقيلة في تركيز أعلى من الحدود القصوى المسموح بها دوليا. وتم مناقشة الأهمية الصحية للمعادن الثقيلة وطرق التحكم فيها.