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ASSESSMENT OF SOME CHEMICAL ENVIRONMENTAL POLLUTANTS IN RAW MILK SAMPLES IN DAKAHLIA GOVERNORATE
(With 2 Tables)

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تقييم بعض الملوثات الكيميائية البيئية فى اللبن الخام في محافظة الدقهلية

يعتبر اللبن الخام من أكثر الأغذية إستهلاكاً نظراً لقيمته الغذائية العالية التي وهبها الله إياها الا أنه قد يكون مسبباً لكثير من الأمراض عن طريق الملوثات البيئية (معادن – مبيدات –مواد سامة وغيرها) أثناء الإنتاج أو النقل أو العرض في الأسواق أو الإستهلاك. لذا أجريت هذه الدراسة لتحديد مدى تواجد بعض المعادن الثقيلة السامة وبعض بقايا المبيدات الحشرية الفوسفورية العضوية ومركبات الكارباميت في عينات اللبن الخام فقد تم تجميع خمسين عينة لبن خام من اسواق مدينة المنصورة وأ يضاً تم تجميع خمسين عينة لبن خام من مزارع لإنتاج اللبن بمحافظة الدقهلية وفحصت هذه العينات كيميائياً لتحديد مدى تواجد بعض المعادن الثقيلة السامة مثل الرصاص والكادميوم بالاضافة الى النحاس وأيضاً قياس بعض بقايا المبيدات الفوسفورية العضوية والكارباميت وقد اسفرت النتائج عن أن متوسط تركيز المعادن الثقيلة) الرصاص – الكادميوم – النحاس (في عينات اللبن المجمع من الاسواق هي (٠.٠٨ ، ٠.٠٦ ، ١.٣٥اجزء من المليون) على التوالي بينما كان متوسط تركيز هذه المعادن الثقيلة في عينات اللبن المجمع من مزارع إنتاج الألبان هي (٠.٠٤ ، ٠.٠٢ ، ١.٠٧اجزء من المليون) على التوالي بينما كان متوسط تركيز بقايا المبيدات الفوسفورية العضوية والكارباميت (الكلوربيرفوس ميثيل – البروفينوس – الكا ربوفيوران – الألديكارب – الميثوميل) في عينات اللبن المجمعة من الأسواق هي (٠.٠٠١٨ ، ٠.٠٠٢١ ، ٠.٠٠١٤ ، غير موجود ،٧. ٠٠٠٠ مجم/كجم وزن) على التوالي ولكن كان متوسط هذه البقايا في عينات اللبن المجمعة من مزارع إنتاج اللبن هي (٠.٠٠٠٦ ، ٠.٠٠١٢ ، غير موجود ، ٠.٠٠٢٨ ، غير موجود مجم/كجم وزن) على التوالي. لذا ننصح بإتباع المبادئ الرئيسية التي تحدد الإستراتيجيات اللازمة لتحسين كفاءة فعالية التحكم الغذائي ، وينبغي على الحكومة أن تقيم متطلبات الأمن الغذائي وتيسر القوانين الصناعية ثم تضمن أن تقابل هذه المتطلبات بالعديد من الخطوات التنظيمية وأن يكون هناك فحص شامل وبشكل دوري على اللبن المعروض للبيع بالأسواق.

SUMMARY

A total of hundred random samples of raw milk were collected from the markets and from dairy farms in Dakahlia Governorate, fifty samples each. All milk samples were analysed for chemical contaminants to determine some heavy metals (lead, cadmium and copper), also to determine some pesticides and carbamate residues (chlorpyrifosmethyl, profenfos, carbofuran, aldicarb and methomyl). The obtained results showed the means concentration of heavy metals (lead, cadmium and copper) in milk samples collected from the markets were 0.08, 0.06 and 1.35 ppm respectively. While the means concentration of lead, cadium and copper in samples collected from dairy farms were 0.04, 0.02 and 1.07 ppm respectively. Regarding to pesticides and carbamate residues (chlorpyrifosmethyl, profenfos, carbofuran, aldicarb and methomyl) their mean concentrations were 0.0018, 0.0021, 0.0014, not detected and 0.0007 mg/kg weight, respectively in milk samples collected from the markets, while the mean values for the samples collected from dairy farms were 0.0006, 0.0012, not detected, 0.0028 and not detected, respectively. So we advice to follow major principles that underlie strategies for improving the efficiency and effectiveness of food control: The efforts are focused on issues that pose the greatest risk. The government must establish food safety requirements, facilitate industry's compliance with these and then ensure that the requirements are through a range of regulatory measures and frequent examination of marketed milk.

Key words: *Milk, heavy metals, pesticides, dairy farms.*

INTRODUCTION

Milk is a basic food in the human diet both in its original form and as various dairy products, it can carry numerous xenobiotic substances (pesticides, drugs, disinfectants, metals and various environmental contaminants), which constitute a technological or risk factors for milk and dairy products (Bluthgen and Heeschen, 1997; Simsek *et al.,* 2000), heavy metals as lead, cadmium and copper refers to any metalic element heavier than iron, they are natural components of the Earth's crust, they are dangerous because they tend to bio-accumulate (Licata *et al.,* 2004).

Heavy metals can enter water supply by industrial wastes, or even from acidic rain breaking down soils and release heavy metal into

water, these contaminants may present a potential hazard for human and animals health if exposure exceeds tolerable levels (Turi-szerletics and Patko, 2008). Heavy metals are persistent types of pollutants which cannot be destroyed by heat treatments or environmental degradation, so their persistence enhance their potential to reach and affect human being (Levensen and Barnard, 1988). Feeding animals with forage produced in contaminated areas results in increasing the concentration of heavy metals in milk and meat (Massanyi *et al.,* 2001). Determination of the residual concentrations of metals in milk could be an important "direct indicator" of the hygienic status of the milk and/or of its derived products, as well as "indirect indicator" of the degree of pollution of the environment in which the milk was produced (Licata *et al.,* 2004) Organophosphorus pesticides are usually esters of phosphoric acid, there is considerable structural diversity in the side chains among the commonly used organophosphorus. The side chains determine the toxicokinetics and toxicodynamics of pesticide poisoning (Moretto, 1998).

Organophosphorus pesticides can appear in milk due to several possible causes: Use of insecticides directly on dairy cattle for ectoparasites control, pasture, or animal feed manufactured from plant material that has been treated with insecticides and use of insecticides in stables or dairy factories. There are several reports of their presence in cow's milk (Kituyi *et al.,* 1997). Residues of organophosphours have been reported in buffalo and pasteurized milk (El-Kohly *et al.,* 2000; Salas *et al.,* 2003). The present work was designed to determine the residual concentration of some heavy metals as lead, cadmium and cupper, also to determine some organophosphorus and carbamat, pesticides residual in raw milk as a servey for the knowledge of their possible hazardous residual limits for human consumption that must be avoided through different safety routs of healthy control measures.

MATERIALS and METHODS

Detection of heavy metals in raw milk samples:
A total of one hundred samples of raw milk were collected in clean polyethylene bottles from different markets in Mansoura City, Dakahlia Governorate and from private dairy farms in Dakahlia Governorate, (fifty samples of each locality). 5ml of each raw milk samples were digested by adding 10ml of conc. HNO_3 solution and perchloric acid (1:1). The samples were digested overnight in a cold

place followed by mild increasing in temperatures till heating at 100C° in water bath for 4 hours, then 5 drops of 30% H_2O_2 were added and heating was continued till the brown nitrous gases were expelled and the specimens become clear. After cooling, each digest was diluted to 25ml with deionized water and filtered through Wattman No. 42 filter paper. The clear filtrate of each sample was kept in refrigerator to avoid evaporation. All samples were analyzed by using flame Atomic Absorption spectrophotometer for determination of lead, cadmium and copper according to AOAC (2004). This was done at Faculty of Science Mansoura University.

Determination of pesticides residues in raw milk Samples:

Fifty ml of milk were blended with ethylacetate for organophosphorus pesticides and with 10ml acetone for carbamate pesticides and sodium sulphate (50gm) was added and the mixture was shaken and then allowed to stand for 2-3 min. The upper layer was decanted, and 50ml aliquot was evaporated to dryness in a rotating evaporator at 35°C. The residue was dissolved in 10ml hexane and then extracted with 2 x 25ml acetonitrile saturated with hexane. Combined acetonitrile phase was evaporated to dryness. The residue was dissolved in 2ml of hexane.

The hexane extract after cleaning up was dried by passing through sodium sulphate anhydrous. The hexane extract was rotary evaporatored to few drops any quantitatively transferred to volumetric tube. The volume was adjusted to lml with hexane. (Naik *et al.,* 2000). This was done at Faculty of Science, Mansoura University.

- Statistical analysis of variance (ANOVA) and t-test was carried out following the method described by (Kirkwood, 1989).

RESULTS

Table 1: Heavy metals concentrations in raw milk samples collected from dairy farms and markets in Dakahlia Governorate.

Raw milk samples	Heavy metals		
	Lead (ppm)	Cadmium (ppm)	Copper (ppm)
Milk samples collected from dairy farms	0.08 ± 0.004	0.06 ± 0.003	1.35 ± 0.06
Milk samples collected from the markets	0.04 ± 0.003	0.02 ± 0.001	1.07 ± 0.2

Table 2: Pesticide residues (mg/kg) in milk samples collected from dairy farms and markets in Dakahlia Governorate.

Class	Pesticide	Raw milk	
		Samples of milk collected from dairy farms.	Samples of milk collected from the markets
Organophosphorus	Chlorpyrifos Methyl	0.0006 ± 0.0001	0.0018 ± 0.0002
Organophosphorus	Profenfos	0.0012 ± 0.0004	0.0021 ± 0.0003
Carbamate	Carbofuran	ND	0.0014 ± 0.0003
Oxime Carbamate	Aldicard	0.0028 ± 0.0003	ND
Oxime Carbamate	Methomyl	ND	0.0007 ± 0.0001

DISCUSSION

Heavy metals are released into the environment by both natural and anthropogenic sources, especially mining, industrial activities and automobile exhausts (for lead). Poison or toxicity in animals occur frequently through exchange and co-ordination mechanisms (Duruibe *et al.,* 2007).

Table 1 showed the mean value of heavy metals (lead, cadmium and copper) concentration in milk samples collected from dairy farms in Dakahlia Governorate were 0.04, 0.02 and1.07 ppm respectively, while the mean concentration value of lead, cadmium and copper in milk samples collected from the markets in Dakahlia Governorate were 0.08, 0.06 and 1.35 ppm respectively. According to the Egyptian standard (2001) the Acceptable permissible limit (APLS) for both lead and cadmium were the same as in milk 0.05 mg/kg, there for the mean values of samples collected from the markets were slightly exceeded the permissible limit and not lied within the APLS. The presence of lead in milk samples may be due to various factors: Automobile vehicles along roads by gasoline burning of tetra ethyl lead content, fodder contamination, from lead based points climatic factors such as winds and the use of lead based pesticide compounds (Buk, 1970). Emam and

El-Nabrawy (2008) found that the mean concentration of lead, cadmium and copper in raw milk collected from Sharkia Governorate were 1.970, 0.353 and 0.025 ppm, respectively. Meanwhile Licata *et al.* (2004) determined lead, cadmium and copper in cow's milk samples which were 1.32, 0.02 and 1.98 mg/kg, as a mean value respectively.

Lead toxicity induced liver and renal dysfunction, the mode of toxic action through the combination with sulfhydrylcarboxy and imidazole containing protein molecules and induced CNS abnormalities as (convulsive seizures, circling, blindness and maniacal behavoirs), anaemia, increased reticulocytes (with basophilic stippling) and substantial functional renal damage with presence of tubular nuclear inclusion bodies **(**Klaassen *et al.,* 1986). Long term exposure to cadmium lead to toxic effects which induced slight anaemia, lung disease and myocardial dysfunctions WHO (1980); INECAR (2000). Zn contained in food interferes with copper absorption system (Klaassen *et al.,* 1986). International Dairy Federation (1991) recorded that 0.001 – 0.005 and 0.002 – 0.0008 mg/kg were the normal range of lead and cadmium in milk respectively.

The results of organophosphorus and carbamate pesticide analysis in the current wark represented by the determination of chlorpyrifos methyl, profenfos, carbofuran aldicarb and methomyl residues in raw milk samples from the markets and milk samples from dairy farms in Dakahlia Governorate: Table 2 showed chlorpyrifos, profenfos, carbofuran, aldicarb and metho myl residues in raw milk samples collected from Dakahlia Governorate markets were with the means of 0.0018, 0.0021, 0.0014, not detected and 0.0007 mg/kg respectively, while samples of milk collected from dairy farms in Dakahlia Governorate were with the means of 0.0006, 0.0012, not detected, 0.0028 and not detected respectively.

Pagliuca *et al.* (2004) found that among more than 100 samples analyzed, 30% were positive to (chlorpyriphos methyl) contamination from eight organophosphorus pesticides, but always below legal limits. These values permit quantification of the residues below legal limit: (10 ppb) for chlorpyriphosmethyl pesticide. The European Commission (2003). The average recoveries of fortified organophosphorus pesticide residues (10 – 50 ppb) ranges from 75.0% to 104.5% were determined in milk samples Schenck and Wagner (1995). Five carbamate insecticides aldicarb, MTMC, carbofuran, carbaryl and MIPC were determined in milk samples and the detected limits of 85 carbamate insecticides were 0.75 – 3.00 ng (Li and Wang, 1997). Both organophosphorus and

carbamate were found in milk samples (cow's raw milk and market), indicated that their misuse in agriculture practices, all means concentration were below the maximum limits permitted by the European Union Mallatus *et al.* (1997).

While organophosphorus and carbamate were not detected in cow's milk samples, by Clascato *et al.* (2002). These results disagree with the obtained showed in Table 2. Di–Muccio *et al.* (1996) determined 24 organophosphorus pesticide residues in milk samples and found levels ranging from 0.02 to 1.11 mg/kg. chlorpyrifos – methyl residues may be present in milk because of their use in crops destined for animal feed such as alfalfa, sorghum, soy and maize (Salas *et al.,* 2003). The presence of these OP- pesticides contrasts with the opinion of Bluthgen and Heeschen (1997), who considered that metabolic breakdown of pesticide is rather quick and that there is only a rare chance to observe their residues in milk. El-Hoshy (1997) has detected the presence of chlorpyrifos – methyl residues in raw milk, also Bolles *et al.* (1999) considered that chlorpyrifos residues are rarely detected in food itmes for example, market milk. Chlorpyrifos is one of the OP-pesticides with higher use in our country INE., (2000). The biosensors developed market it possible to detecte on chlorpyrifos and carbofuran in aqueous solution by cholinesterase sensors (Ivanov *et al.*, 2003), our results were within the permissible limits of The European commission (2003), FAO (2005) and FAO (2008). Pesticides can appear in milk and dairy products due to several possible causes as the use of insecticides directly on dairy cattle for ectoparasite control or animal feed manufactured from plant material that has been treated with insecticides in stables or dairy factories. Pagliuca *et al.* (2004) determined eight pesticide residues in milk, widely used in agriculture. Some of pesticides residue were detected at lower levels, may be due to that were destroyed by acid produced by soil bacteria, reported by UNEP / IOC/ IAEA, (1989). Agricultural production may be adversely affected by flooding associated with natural disasters. When crop fields have been contaminated or damadge, assessments should be carried out to establish measures to reduce the risk of chemicals, hazardous and natural toxins (eg. Delayed harvesting, heat treatment or to assure disposal (FAO, 2005; WHO, 2005).

So we advice to follow major principles that underlie strategies for improving the efficiency and effectiveness of food control: that efforts are focussed on issues that pose the greatest risk. The government must establish food safety requirements, facilitate industry's compliance

with these and then ensure that the requirements are through a range of regulatory measures and frequent examination of marketed milk.

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