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# Chemical Composition of Raw Milk and the Accumulation of Pesticide Residues in Milk Products

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**Abstract:** Milk and dairy products could be contaminated by pesticides during its handling and processing. So, raw milk samples of buffaloes and cows were analyzed for chemical composition and pesticide residues. Buffalo's milk showed higher levels of fat, total protein (T.P), total solids (T.S) and ash than those detected in cow's milk. However, lactose content was higher in cow's milk than those detected in buffalo's milk. Monitoring of pesticide residues in buffalo's and cow's milk was also investigated. Interestingly, non of the raw milk revealed the presence of any organophosphorous pesticides (malathion, profenofos, pirimiphos-methyl and dimethoate). However, organochlorine (OC) pesticides (HCB, lindane, aldrin, heptachlor epoxide, chlordane, endrin and DDT) were detected at a value exceeded the tolerance levels of FAO/WHO. Some residues of pesticides were removed with skim milk and butter milk during the production of cream and butter. Samna and yoghurt were found to contain low levels of OC pesticides due to the effect of heat treatment and the precipitate of residues with the by-product (murta).

**Key words:** Buffalo's milk · Cow's milk · Dairy products · Organochlorine pesticides · Organophosphorous pesticide residues

## INTRODUCTION

Milk is an essential nutritive food for infants and the aged persons. It is a good source for protein, fat and major minerals. These contents vary according to genetics variations among animal species, physical and environmental factors [1,2].

The contamination of milk is considered as one of the main dangerous aspects in the last few years. Milk can be contaminated by residues of organochlorine (OC) and organophosphorous (OP) pesticides [3-7] through a variety of sources. The major source of OC residues is from fodder and soil, while for OP residues is mainly associated with ingestion (through licking) of insecticide used for controlling of parasites on animals [8,9]. The main reasons for environmental contamination by OC compounds are their great production, uncontrolled used, inadequate discharge and persistence in the environment [10]. As a result of using pesticides for controlling plant pests and diseases, their residues are transferred to milk [11].

OC pesticides were widely used worldwide until restrictions were introduced in the late seventies both in Europe and the USA, initially for DDT [7]. Some of these pesticides are still widely used by farmers because of their effectiveness and their broad-spectrum activity [12] and also, are being extensively used in tropical countries in malaria control programs and against livestock ectoparasites and agricultural pests [13].

Persistent OC compounds such as DDT and HCB play an important role in chronic poisoning and take part in a number of pathological processes [14,15]. Fat solubility of these compounds is responsible for their varied concentrations in the tissues and their accumulation in the lipoproteins of the cell membranes, thus changing their structures and permeability [16,17]. OC pesticides are able to significantly decrease the ability of highly purified human natural killer (NK) cells to lyse tumor cells after exposure, ranging from 1 hour to 6 days [18]. Pesticide exposure independently or in synergism with modifiable risk factors, is recognized as an important

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environmental risk factor associated with hemopoetic cancers, cancers of the prostate, pancreas, liver and other body systems [19].

The use of most OC pesticides in Egypt was restricted. Nevertheless, they are present in the environment. Recent studies have been documented their presence both in human blood [20] and foods [3,4,21]. More recent studies find only low levels in food, suggesting that most of the levels found in humans related either to historical use or past human exposures [24,25].

Milk and dairy products can be contaminated by pesticides by improper handling and by feeding the animals on contaminated feeds. This study was conducted to determine the levels of specific pesticides in raw cow's and buffalo's milk samples collected from different animal farms in Egypt in addition to determination of their chemical composition. Also, the effect of processing and heat treatments on milk contents of pesticides and distribution pattern of OC pesticides among some milk products [cream, butter, samna (ghee) and yoghurt] were investigated.

## MATERIALS AND METHODS

### Materials

**Milk:** A total of 120 raw milk samples (1kg each) representing (60 from buffaloes and 60 from cows) were randomly collected from different animal farms in Egypt during the period of 2008 and 2009. Each sample was received in a glass bottle and immediately cooled at -20°C until analyzed.

**Bacterial Strains:** Pure strains belonging to *Streptococcus thermophilus* and *Lactobacillus bulgaricus* were obtained from Egyptian Microbial Collection (EMC) at Microbiological Resources Center (MIRCEN), Faculty of Agriculture, Ain Shams University, Egypt.

**Pesticide Standards:** OC pesticide standards of hexachlorobenzene (HCB), lindane, aldrin, heptachlor, heptachlor epoxide, chlordane, endrin, 1,1,1-trichloro-2,2,bis (p-chlorophenyl) ethane (p.p-DDT), 1-(o-chlorophenyl) -1 - (p-chlorophenyl) - 2,2,2-trichloroethane (o.p'-DDT), 1, 1- dichloro-2,2-bis (p.chlorophenyl) ethylene (p.p'-DDE), 1-(o-chlorophenyl) -1-(p-chlorophenyl) -2,2-di-chloroethane (o.p-DDE), 1-chloro-2,2-bis(p-chlorophenyl)ethane (p.p'-DDD), 1- (o-chlorophenyl) -1-(p-chlorophenyl) -2,2-dichloroethane (o.p'-DDD) and organophosphorous pesticide standards of malathion, dimethoate, profenofos and pirimiphos-methyl were purchased from Chem. Service, Inc. (West Chester, PA).

**Treatments:** Raw milk samples of buffaloes (5.0% fat) and cows (3.5% fat) were exposed to each of the following treatments and manufactured to some products.

**Heat Processing:**

**Pasteurization:** Milk was heated to 73°C for 15 sec and cooled to 10°C.

**Sterilization:** Milk was sterilized in an autoclave,at 121°C.

**Yoghurt:** Milk was heated to 80-82°C for 20 min. and cooled to 40°C. Milk was incubated with 2% starter (1:1 mixture of *S. thermophilus* and *L. bulgaricus*) at 40°C for 3 hr as described by the Egyptian Organization for Standardization [26].

**Cream:** Fresh milk was warmed to 45°C and cream was obtained by using a mechanical separator.

**Butter:** Butter was obtained by warming the milk and separated by using a mechanical separator to obtain cream and churned by using churner for obtaining butter [27].

**Samna (Ghee):** Samna was prepared from cream according to the method of El-Sadek *et al.* [28].

### Methods of Analysis

**Chemical Analysis:** Fat, total nitrogen (T.N), lactose content, total solids (T.S) and ash were determined according to AOAC methods [29]. The pH values were measured by using Knick-Digital pH meter Model 646.

**Pesticide Residues Analysis:** Pesticide residues were extracted from different samples under investigation by AOAC methods [29] and Pesticide Analytical Manual [30]. Aliquots of 1-2 μl of extracts were injected into a Hewlett Packard GC Model 5890 equipped with $Ni^{63}$ Electron Capture Detector (ECD) and Flame Ionization Detector (FID) and fitted with HP- 101 capillary column (Cross linked methyl silicon Gum), 30 m length, 0.25 mm diameter and 0.25 μm film thickness. The oven temperature was programmed to start by 160°C and raised to 220°C with rate of 5°C/min and was held for 30 min. Injection and detector temperatures were 220°C and 300°C, respectively.

To determine method quality, a recovery study was performed on milk samples and its products (cream, butter, samna and yoghurt) that were spiked by the used pesticides. After extraction, the samples were analyzed according to the aforementioned method. The recovery values were calculated from calibration curves constructed from the concentrations and peak areas of the obtained chromatograms with standards of OC and OP pesticide. Blank analysis was performed in order to check interference from the sample. Mean recoveries ranged from 90 to 94% with S.D < 6 indicating excellent repeatability and the limit of detection (LOD) was 0.001 mg/kg.

## RESULTS

**Chemical Composition of Buffalo's and Cow's Milk:** Chemical composition of buffalo's and cow's milk collected from different animal farms in Egypt was determined and the results were presented in Table 1. Buffalo's milk contained fat (5.70%), T.P (3.60%), ash (0.76%) and T.S (13.40%) at levels higher than those detected in cow's (3.2, 3.2 and 12.1%, respectively) milk. In contrast, lactose content in buffalo's milk (4.80%) was lower than that determined in cow's milk (5.0%). Acidity and pH values in both species, were approximately similar.

Table 1: Chemical composition % of buffalo's and cow's milk (Mean ±SD)

| Analysis | Buffalo's milk | Cow's milk |
|---|---|---|
| Acidity | 0.16±0.09 | 0.16±0.08 |
| pH value | 6.70±1.25 | 6.60±1.10 |
| Fat | 5.70±0.86 | 3.20±0.95 |
| T.P | 3.60±0.95 | 3.20±0.85 |
| Ash | 0.76±0.14 | 0.65±0.25 |
| T.S | 13.40±1.50 | 12.10±1.80 |
| Lactose | 4.80±0.55 | 5.00±0.60 |

T.P = Total Protein, T.S = Total Solids

**Pesticide Residues in Raw Milk from Different Animal Farms:** Pesticide residues in buffalo's and cow's raw milk samples collected from different animal farms were tested during the period of 2008 and 2009. Results showed that different residues were found and presented in Table 2. About 50.0 and 43.30% of the detected residues were lindane at mean levels of 0.046 and 0.036 mg/kg fat basis in buffalo's and cow's milk, respectively. The presence of lindane in the collected samples were above the maximum residue limit of international organizations (0.01 mg/kg fat).

For OC analysis, HCB was found in 41.7 and 36.7% of the collected buffalo's and cow's milk samples, respectively. The mean concentration of HCB in buffalo's milk was higher (0.162 mg/kg fat) than those detected with cow's milk samples (0.150 mg/kg fat). Aldrin results showed that 33.3% (mean value 0.066 mg/kg fat) of buffalo's and 26.7% (mean value 0.05 mg/kg fat) of cow's milk contained this compound. The average levels of the detected aldrin in raw milk samples were high.

Table 2: Pesticide residues (mg/kg fat basis) in milk samples

| | Frequency (+) ve samples | | | | | | MRLs FAO/WHO | |
|---|---|---|---|---|---|---|---|---|
| | Buffalo's milk | | | Cow's milk | | | | |
| Pesticide Name | % (+) ve | Mean ± SD | Range (+) ve samples | % (+) ve | Mean ± SD | Range (+) ve samples | 1993 | 2008 |
| HCB | 41.7 | 0.162±0.08 | 0.081-0.186 | 36.7 | 0.150±0.08 | 0.091-0.180 | - | - |
| Lindane | 50.0 | 0.046±0.02 | 0.021-0.082 | 43.3 | 0.036±0.02 | 0.012-0.046 | 0.010 | 0.010 |
| Aldrin | 33.3 | 0.066±0.04 | 0.040-0.080 | 26.7 | 0.050±0.02 | 0.030-0.072 | 0.006 | 0.006 |
| Heptachlor | 8.3 | 0.032±0.02 | 0.012-0.042 | 10.0 | 0.022±0.01 | 0.016-0.030 | Total= 0.006 | Total= 0.006 |
| H. epoxide | 25.0 | 0.064±0.03 | 0.044-0.078 | 20.0 | 0.076±0.04 | 0.066-0.082 | | |
| Chlordane | 16.7 | 0.022±0.02 | 0.010-0.036 | 20.0 | 0.016±0.01 | 0.010-0.022 | 0.002 | - |
| Endrin | 20.0 | 0.020±0.01 | 0.016-0.042 | 16.7 | 0.012±0.01 | 0.010-0.016 | 0.0008 | - |
| p.p'-DDT | 13.3 | 0.022±0.01 | 0.011-0.030 | 16.7 | 0.032±0.02 | 0.022-0.048 | Total = 0.050 | Total = 0.020 |
| o.p'-DDT | 10.0 | 0.006±0.02 | 0.001-0.009 | 16.7 | 0.004±0.01 | 0.002-0.006 | | |
| p.p'-DDE | 18.3 | 0.004±0.03 | 0.030-0.006 | 16.7 | 0.028±0.01 | 0.016-0.040 | | |
| o.p'-DDE | 23.3 | 0.060±0.03 | 0.040-0.080 | 20.0 | 0.080±0.06 | 0.009-0.160 | | |
| p.p'-DDD | 26.7 | 0.016±0.01 | 0.009-0.020 | 23.3 | 0.070±0.04 | 0.001-0.096 | | |
| o.p'-DDD | 26.7 | 0.014±0.01 | 0.010-0.030 | 23.3 | 0.009±0.01 | 0.001-0.016 | | |

% (+) ve = Percentage of positive samples

Table 3: Effect of manufacturing processes on the distribution of some OC pesticide levels (mg/kg fat basis) in buffalo's milk and its products *

| | | Heat treatment | | Manufacturing process | | | |
|---|---|---|---|---|---|---|---|
| Pesticide name | Raw milk | Steriliz-ation | Pasteuri-zation | Cream | Butter | Samna | Yoghurt |
| HCB | 0.143 | 0.122 | 0.132 | 0.138 | 0.130 | 0.092 | 0.123 |
| Lindane | 0.037 | 0.030 | 0.033 | 0.034 | 0.026 | 0.014 | 0.034 |
| Aldrin | 0.032 | 0.026 | 0.028 | 0.028 | 0.021 | 0.013 | 0.030 |
| Heptachlor | - | - | - | - | - | - | - |
| H. epoxide | 0.042 | 0.033 | 0.036 | 0.038 | 0.029 | 0.020 | 0.038 |
| Chlordane | 0.023 | 0.020 | 0.022 | 0.020 | 0.016 | 0.009 | 0.020 |
| Endrin | - | - | - | - | - | - | - |
| p.p'-DDT | 0.042 | 0.034 | 0.038 | 0.038 | 0.034 | 0.021 | 0.036 |
| o.p'-DDT | 0.006 | - | 0.004 | 0.005 | 0.004 | 0.002 | 0.005 |
| p.p'-DDE | 0.034 | 0.027 | 0.030 | 0.030 | 0.026 | 0.018 | 0.031 |
| o.p'-DDE | 0.043 | 0.039 | 0.040 | 0.038 | 0.032 | 0.026 | 0.039 |
| p.p'-DDD | 0.001 | - | - | - | - | - | - |
| o.p'-DDD | 0.014 | 0.012 | 0.012 | 0.011 | 0.008 | 0.004 | 0.008 |

(-) = Below Limit of Detection (LOD) = 0.001 mg/kg fat basis, * = OP not detected in all of the tested samples

Table 4: Effect of manufacturing processes on the distribution of some OC pesticide levels (mg/kg fat basis) in cow's milk and its products *

| | | Heat treatment | | Manufacturing process | | | |
|---|---|---|---|---|---|---|---|
| Pesticide name | Raw milk | Steriliz-ation | Pasteur-ization | Cream | Butter | Samna | Yoghurt |
| HCB | 0.093 | 0.079 | 0.080 | 0.089 | 0.080 | 0.060 | 0.083 |
| Lindane | 0.024 | 0.016 | 0.021 | 0.022 | 0.016 | 0.011 | 0.022 |
| Aldrin | 0.021 | 0.016 | 0.018 | 0.019 | 0.014 | 0.009 | 0.019 |
| Heptachlor | - | - | - | - | - | - | - |
| H. epoxide | 0.060 | 0.021 | 0.036 | 0.050 | 0.039 | 0.026 | 0.055 |
| Chlordane | 0.015 | 0.013 | 0.014 | 0.013 | 0.010 | 0.006 | 0.012 |
| Endrin | - | - | - | - | - | - | - |
| p.p'-DDT | 0.047 | 0.022 | 0.025 | 0.038 | 0.032 | 0.014 | 0.042 |
| o.p'-DDT | 0.004 | - | - | 0.003 | 0.002 | - | 0.003 |
| p.p'-DDE | 0.022 | 0.018 | 0.020 | 0.020 | 0.016 | 0.010 | 0.018 |
| o.p'-DDE | 0.060 | 0.025 | 0.050 | 0.055 | 0.045 | 0.037 | 0.049 |
| p.p'-DDD | 0.004 | - | - | - | - | - | - |
| o.p'-DDD | 0.011 | 0.006 | 0.009 | 0.008 | - | - | 0.009 |

(-) = Below Limit Of Detection (LOD) = 0.001 mg/kg fat basis, * = OP not detected in all of the tested samples

Results revealed the presence of heptachlor at 8.3% and heptachlor epoxide at 25.0% in buffalo's milk as well as 10.0 and 20.0% in cow's milk samples, respectively. The sum of heptachlor and heptachlor epoxide (0.096 and 0.098 mg/kg in buffalo's and cow's milk, respectively).

Also, Table 2, shows that, chlordane was detected in buffalo's milk samples with an average of 0.022 mg/kg fat in buffaloes and 0.016 mg/kg fat in cows. Frequency positive samples was 16.7 and 20.0 % in buffalo's and cow's milk samples, respectively. Mean concentration of chlordane in our study was relatively high. Regarding to endrin, it was found in 20% of buffalo's milk samples (an average 0.020 mg/kg fat) and 16.7% (an average of 0.012 mg/kg fat) in cow's milk samples.

This study revealed the presence of DDT and its derivatives (p.p'-DDT; o.p'-DDT; p.p'-DDE; o.p'-DDE; p.p'-DDD and o.p'-DDD). As shown in Table 2, an average of 0.122 mg/kg fat and 0.223 mg/kg fat of sum DDT were recorded for raw buffalo's and cow's milk samples, respectively. Interestingly, non of the buffalo's or cow's milk samples revealed the presence of any OP pesticides (malathion, profenofos, pirmiphos-methyl and dimethoate).

**Pesticides Distribution among Different Milk Products:** Buffalo's and cow's milk samples were collected to manufacture different products, i.e., pasteurized and sterilized milk, cream, butter, samna and yoghurt. The obtained results in Tables 3 and 4 indicated the presence of pesticide residues in raw milk before manufacture, except heptachlor and endrin, which were not detectable in either buffalo's or cow's milk samples. The highest residue concentration detected in raw milk was DDT and its derivatives (p.p'-DDT, o.p'-DDT, p.p'-DDE, o.p'-DDE, p.p'-DDD and o.p'-DDD), which recorded 0.140 and 0.148 mg/kg fat basis in buffalo's and cow's milk samples, respectively. HCB residues recorded 0.143 mg/kg fat for buffalo's milk and (0.093 mg/kg fat) for cow's milk. Chlordane residues recorded the lowest level of pesticides in buffalo and cow samples (0.023 and 0.015 mg/kg fat, respectively). On the other hand, moderate levels of OC were also recorded. Aldrin (0.032 and 0.021 mg/kg fat basis, respectively), lindane (0.037 and 0.024 mg/kg fat basis, respectively) and heptachlor epoxide (0.042 and 0.060 mg/kg fat basis).

The effect of heat treatments, i.e., sterilization and pasteurization on the concentrations of pesticide residues in both buffalo's and cow's milk was studied and data was illustrated in Tables 3 and 4.

The skimming of buffalo's and cow's milk led to slight reduction in the analyzed pesticide's concentration in skim milk (Tables 3 and 4). The reduction levels in buffalo's and cow's milk were about 3.5 and 4.3%, 8.1 and 8.3%, 12.5 and 8.3%, 9.5 and 16.7%, 13.0 and 8.3% and 12.9 and 16.0% for HCB, lindane, aldrin, heptachlor epoxide, chlordane and total DDT, respectively.

Butter from churning buffalo's or cow's cream contained lower concentrations of pesticides than that detected in their creams. Data in Tables 3 and 4 indicated that, the reduction levels of HCB, lindane, aldrin, heptachlor epoxide, chlordane and total DDT in butter from contaminated buffalo's and cow's cream were about 5.8 and 10.1%, 23.5 and 27.3%, 25.0 and 26.3%, 23.7 and 22.0%, 20.0 and 23.1% and 21.3 and 23.4%, respectively.

The production of samna from buffalo's and cow's butter reduced the levels of pesticide residues (Tables 3 and 4). The reduction levels of HCB, lindane, aldrin, heptachlor epoxide, chlordane and total DDT in samna from buffalo's and cow's butter samples were 29.2 and 25.0%, 46.2 and 31.3%, 38.1 and 35.7%, 31.0 and 33.3%, 43.8 and 40.0% and 31.8 and 35.8%, respectively Tables 3 and 4 also show that the manufacture of yoghurt from buffalo's and cow's milk resulted in a decreased levels of the studied pesticides. The reduction of HCB, lindane, aldrin, heptachlor epoxide, chlordane and total DDT in yoghurt from buffalo's and cow's milk were about 14.0 and 10.8%, 8.1 and 8.3%, 6.25 and 9.50%, 9.50 and 8.3%, 13.0 and 20.0% and 15.0 and 18.2%, respectively.

## DISCUSSIONS

The obtained results of chemical composition of buffalo's and cow's milk were in agreement with that reported by Dabiza *et al.* [34]. However, buffalo's milk samples in this study were found to contain fat, lactose and T.P at values lower than those detected by Castagnetti *et al.*[35] who reported that fat, lactose and protein were 8.54, 5.12 and 4.50%, respectively. On the other hand, fat and T.S, in buffalo's milk in the present study were lower than those detected by Kholif, *et al.* [1] and Abou-Arab [2] who reported that fat and T.P. contents were 6.0 and 15.23% and 5.9 and 14.98%, respectively. In contrast, T.P, in the present investigation was higher than those reported by Kholif (3.23% in buffalo's and 3.02% in cow's milk) and Abou-Arab (3.41% in buffalo's milk) studies.

With respect to pesticide residues in raw milk samples. Lindane mean values in current investigation are higher than those values recorded by Waliszewski *et al.* [9], Heck *et al.* [36] and Darko and Acquaah [6] who detected mean values, 0.030, 0.005 and <LOD, respectively. However, our values are lower than those detected by Battu *et al.* [5]. Also, the frequency positive samples of lindane in our study was lower than those reported by Waliszewski *et al.*[9] and Battu *et al.* [5], which were 80 and 53.3%, respectively.

The frequency positive samples of HCB in the current investigation was lower than those detected by Waliszewski *et al.* [9], Campay *et al.* [37] and Heck *et al.* [36] who reported that the frequency positive samples were 84.3 (mean value 0.014 mg/kg fat), 94-100 and 100% (mean value 0.003 mg/kg fat), in this order.

Similar high level of aldrin was recorded by John *et al.* [37] who found aldrin in buffalo's milk at concentration 0.15 mg/kg fat. In contrast, lower levels of aldrin were determined in the bovine milk samples, which were 0.002 and 0.003 mg/kg fat, respectively [36,40]. Non of the liquid milk samples revealed the presence of aldrin at their detection limit of 0.01 mg/kg with the investigations of Waliszewski *et al.* [9] and Darko and Acquaah [6]. Similar results of heptachlor were obtained by John *et al.* [38] who found its residues in buffalo's milk at level 0.15 mg/kg which exceeded the tolerance limit. In contrast, heptachlor was not detected above the detection limit of 0.002 mg/kg in cow's milk samples analyzed by Waliszewski *et al.* [9]. However, the author found heptachlor epoxide in 5% of the collected samples at mean level 0.007 mg/kg. Mean concentration of chlordane in our study is exceeded the tolerance level of 0.002 mg/kg reported by FAO/WHO [31]. Also the values of endrin exceeded the tolerance limit of 0.8 μg/kg recorded by FAO/WHO [32].

The concentration of DDT and its derivatives was similar to the levels recorded by Waliszewski *et al.* [9].

On the other hand, the values of total DDT in the present study were higher than those recorded by John *et al.*[37], Battu *et al.* [5], Heck *et al.* [35] and Darko and Acquaah [6]. However, values of sum DDT in current study are lower than those reported for raw milk from some developing countries, for example, Uganda 3.24 mg/kg, Nigeria 3.83 mg/kg, India 6.55 mg/kg, Kenya 6.99 mg/kg, South Africa 20.10 mg/kg and Ethiopia 7.75 mg/kg [39].

Interestingly, non of the buffalo's or cow's milk samples revealed the presence of any OP pesticides (malathion, profenofos, pirimiphos-methyl and dimethoate). These results could be attributed to the high water solubility of these compounds. Therefore, animals secrete most of these chemicals in the urine and feces [40].

All of the OC pesticides detected in the present samples have been used in Egypt during the last two decades [32]. The results of the present investigation are contrary to earlier reports in Egypt [22,42]. The study carried out during 1991 indicated the change in the concentration of pesticide residues in milk. The analysis of 240 samples of buffalo's and cow's milk showed the presence of mean values, 0.074 mg/kg fat basis lindane in 62.1%, HCB 0.289 in 51.7%, heptachlor 0.178 in 24.6%, aldrin 0.091 in 18.8%, γ-chlordane 0.031 in 27.1% and total DDT 0.282 mg/kg fat basis in 46.8%. In 1983, a study showed endrin at 0.02 mg/kg fat in Kalubia (Egypt). The good news is that the levels of pesticides detected in milk in 2008 and 2009 were very low compared with 1991 and 1983. This reduction in the variety of chlorinated pesticides indicates a replacement process as regulations were implemented.

Results of pesticides distribution among different milk products showed the efficient role of sterilization process (121°C/5min) on the degradation or elimination of pesticide residues. These showed reduction percent in the concentration of pesticides in both buffalo's and cow's milk. On the other hand, pasteurization proved the least effective These results are in agreement with those reported by Abou-Arab [22] who showed that sterilization at 121°C for 15 min. showing 83.25, 91.67 and 68.70% loss with β-BHC, lindane and p.p'-DDT, respectively. The higher reduction may be due to the long time of treatment. In addition, Rachev *et al.* [43] reported that pasteurized raw milk at 93°C or 100°C for few seconds had a little effect on β-BHC and p.p'-DDT. The mean concentrations of OC pesticides in raw, pasteurized and UHT milk samples are reported by Heck *et al.* [35]. They found that One-way ANOVA revealed that o.p'-DDD and total DDT levels were significantly higher in raw milk than in pasteurized and UHT milk, while p.p'-DDD was significantly higher in UHT than in raw milk. On the other hand, Costabeber *et al.* [44] evaluated OC pesticides in UHT milk from Santa Maria (Brazil). They found lindane (0.01 mg/kg fat) and HCB (0.001 mg/kg fat). In other study, pasteurized milk was analyzed in Argentin to determine OC pesticides [45]. Mean concentration (mg/kg fat) were 0.0068, 0.04521, 0.0549, 0.0388, 0.0232 and 0.990 with HCB, γ-HCH, heptachlor and heptachlor-epoxide, aldrin, chlordane and DDT (sum of isomers), respectively. These results proved the efficient role of heat treatments on the degradation of pesticides. OC pesticides and their residues are highly lipophilic nature and are hardly metabolized [46]. Hence, it may easily concentrate in fatty foods (such as milk products) leading to bioconcentration and biomagnifications through chain [6]. Thus, their contents in dairy products reflect the regional environmental contamination and may be of great value for scientific and public health knowledge.

The skimming of buffalo's and cow's milk led to slight reduction in the analyzed pesticide concentration with skim milk. These results coincide with those reported by Abou-Arab [22] who found that skimming of milk led to slight reduction in β-BHC, lindane and DDT. In contrast, higher reduction levels in lindane and DDT were reported by El-Alfy [47]. These differences in the reduction levels may be due to the skimming process and the higher losses of fat in the skim milk.

Analysis of butter from churning buffalo's or cow's cream revealed that it contained lower concentrations of pesticides (HCB, lindane, aldrin, heptachlor epoxide, chlordane and total DDT) than that detected in their creams. Similar results were obtained by Langlois *et al.* [48] and Waliszewski *et al.* [9]. These results could be scribed to the transfer of most fat globule membrane to the buttermilk carrying considerable portions of pesticides. Of the HCH isomers, mainly lindane was detected and it differs from DDT in its physicochemical properties with respect to vapor pressure, water and fat solubility. Biegel [49] revealed a high vapor pressure for lindane in comparison to that of DDT. Moreover, DDT is practically insoluble in water in comparison to lindane. DDT has high lipophilicity of approximately 100,000 ppm compared to lindane [5]. Moreover, the manufactured butter was incorporated with sodium chloride and cured to 2.2 and 1.0%, respectively and had about 16% water. All of these factors may have been responsible for its low frequency of occurrence and low levels of lindane in butter in comparison to liquid milk. Generally, the churning process led to remove part of pesticide residues into butter milk.

The production of samna from buffalo's and cow's butter reduced the levels of pesticide residues. This reduction may be due to the heat treatment during butter boiling off as well as the precipitate of the residues with the by-product (murta). Similar findings were reported by Abou-Arab [4].

The manufacture of yoghurt from buffalo's and cow's milk resulted in a decreased levels of the studied pesticides. This reduction may be due to the heat treatment of milk (80-82°C for 20 min.) as well as the activity of yoghurt starter culture (*S. thermophilus* and *L. bulgaricus*). It was reported that certain strains such as Lactic acid bacteria are able to alter DDT and some others of pesticides [23,50]. On the other hand, El-Alfy [47] found higher reduction of lindane (34%) than the reduction observed in current study. The influence of yoghurt starter without heating process on some pesticides such as β-BHC, DDT and lindane was studied by Abou-Arab [22] who reported that the activity of starter led to reduction of the pesticides. On the other hand, yoghurt samples were analyzed by Darko and Acquaah [6] and found that. the detected levels of aldrin, dieldrin, DDT, DDE and lindane were below the extraneous maximum levels of 500 μg/kg recorded by FAO/WHO [31]. These results confirmed our current data.

It could be concluded that OC pesticide residues were detected in buffalo's and cow's milk which were collected from different animal farms. In most cases, the values of detected OC pesticides were exceeded the tolerance levels of FAO/WHO. Interestingly, non of the raw milk revealed the presence of any OP pesticides (malathion, profenofos, pirmiphos-methyl and dimethoate). Heat treatments such as sterilization and pasteurization showed the efficient role on the degradation of the pesticide residues. OC pesticides were fat soluble so, their residues were found in high fat dairy products such as cream and butter. Residues of some pesticides removed with skim milk and butter milk due to the association of residues with the phospholipids in milk fat [51]. Samna contained lower levels of OC pesticides because of the heat treatment and the precipitate of residues with the by-product (murta). The reduction of OC pesticides in yoghurt production may be due to the heat treatment of milk and the activity of their starter. Generally, the consumption of milk as milk products may be safer than raw milk.

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