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# CHEMICAL CONSTITUENTS AND PESTICIDE RESIDUES LEVELS IN HUMAN,COW AND BUFFALOES MILK

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## ABSTRACT

Milk and its products are a main constituent of the daily diet ,especially for vulnerable groups such as infants, school-age children, pregnant, lactating women and old age.

A total of 128 samples were collected at random from different sources and sites in Egypt. Seven samples were human milk, 67 were cows milk and the rest were Buffaloes milk. All the tested samples were analysed for the detection of fat, sugar, protein and ash. Data indicate that there was a great difference in their constituents .Buffaloes milk headed all the tested milk samples in its contents of fat, protein and total ash, while human milk had a greatest percentage in sugar.

All the tested samples of buffaloes and cow milk contained DDT and/or its metabolites, lindane, endrin, dieldrin,while only 85 % of the tested human milk samples contained one or more of the investigated pesticides

The presence of these residues varied between traces to 11.9 ppm. in buffaloes and cow milk ,while the maximum residue level was 1.26 ppm in the case of human milk.The level of pesticide residues was related to the fat content of the tested milk. Buffaloe milk headed all the other tested milk in its content of pesticide residues followed by cow and finally by human milk.

## INTRODUCTION

Several limited monitoring programs received an extensive investigation in order to detect residues from organochlorine compounds in milk,Goursaud *et al* 1972, Goursaud 1976, Fries and Marrow 1976,Uhnak *et al* 1978 , Dogheim *et al* 1988. Abdel-Fatah *et al* 1993, Riva and Anadon 1991, Frank *et al.*, 1970, 1975, 1979 and 1985 Frank and Braun, 1989.

Riva and Anadon 1991 reported that by determining the pesticide residues in 460 samples of cow milk, all samples were contaminated by one or more of the investigated pesticides. Most of the milk samples were contaminated with HCH isomers, DDT isomers, Aldrin and Dieldrin. Lindane was found in all analyzed samples whereas, endrin, heptachlor, heptachlor epoxide, endosulfan, methoxi- chlor and mirex were not detected in any sample.

Now measurable amounts of pesticides residues find their way to pollute our food. Organochlorine pesticides were detected in human milk samples in Finland (Russalo-Rauhaman *et al.*, 1988); in Italy (Dommarco *et al.*, 1987); in Norway (Skaare *et al.*, 1988); in Sweden (Noren and Sjovall, 1987); in Kenya (Kanja *et al* ., 1992); in Zimbabwe (Chikuni *et al.*, 1991); in Germany (Ehrenstorfer *et al* ., 1991); in Yugoslavia (Krauthacker, 1991); in Egypt (El- Sheikh *et al.*, 1989 and Dogheim *et al.*, 1991) ; in Canada (Frank *et al.*, 1985); in France (Bordet *et al.*, 1993) and in Brazil (Beretta and Dick, 1994).

Data also indicate that cow milk is also polluted by organochlorine residues as reported before by Jahn *et al.*, 1991; Saleh 1991 (in USA); Juszkiewics and Niewiadowska 1984 (in Poland); El-Alfy 1981; Abdel-Gawaad and Shams El-Din 1989 (in Egypt); Mukherjee and Gopal 1993 (in Delhi); Trotter and Dickerson 1993 (in United States) and Kristoforovic, Inic and Slavic 1995 (in Yugoslavia).

## MATERIALS AND METHODS

A total of 128 samples were collected at random from different sources and sites in Egypt. Twenty seven samples were human milk, 67 were cow milk and the rest were buffaloes milk.

The samples were kept in deep-freezer under -18°C until analysis.

For the determination of protein, Ash, fat and lactose,the same methods reported by.FAO 1986 were conducted.

### Standards used:

The following primary standards were obtained from the repository of the U.S. Environment Protection Agency at Research Triangle Park, N.C. These standards included, aldrin, dieldrin, BHC, chlordane, DDE, DDD, DDA, DDT, endrin, heptachlor and lindane.

The working standard solutions of three concentrations were prepared daily 1,2 and 4 nanogram per microliter with pesticide quality hexane solvent.

**Extraction and clean up:**

One step extraction and clean up was conducted according to the modified multiresidue method of Stijve and Cardrnale, 1974 as reported by Abdel-Fatah *et al.*, 1992.

**Detection:**

Hewlett Packard , Model (HP5890 A) programable gas chromatograph with HP -101 methyl silicone fluide

columns ( 25 x 0.2 mm ), equipped with an electron capture detector was used.

**Operating conditions:** Initial temperature 150°C, temperature rate 5°C per min., final oven temperature 220°C, detector temperature 300°C and flow of carrier gas 40 ml $N_2$ per min.

## RESULTS

Chemical constituents of human, cow and buffaloes milk indicated that the percentage of fat in human milk varied between 3.67- 3.79%, while it was 3.89-4.12 and 7.58-7.98 for cow and buffaloes samples respectively.Buffaloes milk headed all the tested milk in its content of protein (3.98-4.00%), followed by Cow milk (3.27-3.31%) and by human milk (1.89-2.03 %). Human milk headed all the other tested milk in its sugar content (6.19-6.21%) followed by buffaloes milk (5.01-5.19%),and by cow milk (4.99-5.09% ). The total content of ash was 0.68, 0.31, 0.78% for cow, human and buffaloes milk respectively (table 1).

**Table 1:** Chemical constituents of different types of milk.

| Type of milk | Mean percentage | | | |
|---|---|---|---|---|
| | Ash | Fat | Protein | Lactose |
| Cow | 0.67 | 3.65 | 3.39 | 5.04 |
| Buffalo | 0.86 | 7.51 | 4.79 | 4.60 |
| Human | o.32 | 3.69 | 2.25 | 6.33 |

The data in table (2) illustrated that endrin and dieldrin were not detected, while total DDT had the maximum residue level (0.3215 ppm). All residues were below the MRL's. Chlordane residues were detected at an exceptionally high level followed by aldrin and lindane.

**Table 2:** Average estimated chlorinated hydrocarbon insecticides in Cow milk.

| Residues | Mean ± S.E ppm (ug/kg) | Residues range (ppm) | Incidence % | MRL or ERL mg/kg |
|---|---|---|---|---|
| Aldrin | 0.023±0.0189 | 0.00-0.1138 | 56 | 0.006* |
| Chlordane | 0.098 ±0.0325 | 0.00-1.2357 | 67 | 0.002 |
| Dieldrin | ND | - | 0 | 0.006* |
| Total DDT | 0.312±0.5027 | 0.00-3.6721 | 24 | 0.050 |
| Endrin | ND | - | 0 | 0.008 |
| Heptachlor | 0.107±0.0652 | 0.00-0.9753 | 31 | 0.006 |
| Lindane | 0.004±0.0031 | 0.00-0.0214 | 47 | 0.010 |

ND= Not detectable residues ,MRL = Maximum residues limits, ERL = extraneous residues limits, * ERL for sum. Aldrin + dieldrin

Results in table (3) show that heptachlor had the maximum level (0.3981±0.2793) in buffaloes milk followed by the total DDT ,while dieldrin and endrin were traces (less than 0.001ppm).Chlordane residues were the most incidental (65%) while endrin or dieldrin were the lowest one, 8 and 10 % respectively.

**Table 3:** Percentages estimated chlorinated hydrocarbon insecticides in Buffaloes milk samples.

| Residues | Mean ± S.E. ppm | Residues range (ppm) | incidence % | MRL. or ERL mg/kg |
|---|---|---|---|---|
| Aldrin | 0.032±0.0291 | 0.0 - 0.1138 | 44 | o.oo6* |
| Chlordane | 0.041±0.0385 | Traces -1.4275 | 65 | 0.002 |
| Dieldrin | traces | 0.0 -Traces | 10 | 0.006 |
| Total DDT | 0.371±0.6011 | Traces -4.3753 | 32 | 0.050 |
| Endrin | traces | 0.0 -Traces | 8 | 0.008 |
| Heptachlor | 0.398±0.2793 | 0.0 -0:8898 | 25 | 0.006 |
| Lindane | 0.005±0.0046 | Traces -0.0300 | 54 | 0.010 |

ND= Not detectable residues ,MRL = Maximum residues limits, ERL= extraneous residues limits, * ERL for sum. Aldrin + dieldrin

**Table 4:** Average estimated chlorinated hydrocarbon insecticides in Human milk samples.

| Residues | Mean ± S.E. ppm | Residues range (ppm) | incidence % | MRL or ERL mg/kg |
|---|---|---|---|---|
| Aldrin | 0.003 ± 0.0017 | 0.00-000112 | 28 | 0.006 |
| Chlordane | 0.003 ± 0.0023 | 0.00-0.0143 | 14 | 0.002 |
| Dieldrin | Traces | 0.00- Traces | 14 | 0.006 |
| Total DDT | 0.056± 0.0096 | Traces-0.5107 | 100 | 0.050 |
| Endrin | 0.011± 0.0027 | 0.00-0.0340 | 28 | 0.008 |
| Heptachlor | 0.008± 0.0012 | 0.00-0.0340 | 85 | 0.006 |
| Lindane | 0.008± 0.0309 | 0.00-0.0309 | 71 | 0.010 |

ND= Not detectable residues ,MRL = Maximum residues limits, ERL= extraneous residues limits, * ERL for sum. Aldrin + dieldrin

Table (4) indicates that all human milk samples contained DDT residues or its isomers , at a level of 0.0569 ± 0.0096 ppm which can be considered as the highest level between all detectable residues. .Chlordane and dieldrin residues were detected in 14 % of the tested samples. Dieldrin was detected in traces while chlordane level was 0.0037 ppm.

## DISCUSSION

From the above results it is clear that all sources of milk contained pesticide residues.

The MRLs or ERLs established by the Codex Alimentarius commission (CAC) of the FAO/WHO food standard programs, illustrated that all the determined residues in different kinds of milk were under these limits.

These results agreed with the results reported by Dogheim et al, 1991 and confirmed with the results of El-Sheikh et al, 1989 and Abdel-Fatah et al 1993.

The global perspective of organochlorine pesticide

residues in dairy milk as compiled by GEMS/food programme reveals from the data submited by reporting countries,that in general,milk contains,the highest residue levels compared to any other food group. However, these residues are generally below MRL's with a few exceptions and are slowly declining in most developed countries such as USA, Canada and Netherlands as well as some developing countries. There is no evidence of changes in these levels with time as the general trend is maintained except for Germany,Japan and some developing countries,where the level is increasing at a high rate (GEMS,1991).

The organochlore insecticides detected in this study are in accordance with previous studies conducted in Egypt in general for most pesticides.However,residues for some pesticides ,that were not used extensively in Egypt( i.e. heptachlor, chlordane) at any time,were detected at an exceptionally high level in all sources of milk tested.This could only be explained by the contamination of animal feeds and concentrates used.As the relation between the levels of chlorinated hydrocarbons in feed and that in milk is linear. However at lower levels in feed, the level in milk could be as much as double or more that in feed, Witt *et al.*; 1966 and Matsumura 1976. These feeds and concentrates are being imported from countries that used or may be are still using these pesticides.

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