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Distribution of some persistent organic pollutants (POPs) in cow's milk in Egypt

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ABSTRACT

The concentrations of 11 organochlorine pesticides residues were determined in 100 samples of cow's milk collected from five districts of El-Qalubiya Governorate, Egypt during March to April, 2011. The most predominant organochlorine compounds in cows milk were p,p'-DDD (49%) and endrin (42%) with a mean value of 0.513±1.04 and 0.457±0.566 ng/ml, respectively. All samples were contaminated with one or more of the investigated pesticides. From public health point of view, the observed levels of OCPs residues in cow's milk's in this study do not pose a serious health risk to the consumers. © 2012 Trade Science Inc. - INDIA

KEYWORDS

Organochlorine pesticides Residues;
POPs;
Milk;
Contamination.

INTRODUCTION

Persistent organic pollutants (POPs) are synthetic chemical substances with unique and harmful characteristics. They pose severe risks to human health and the environment due to their toxicity, their persistence, their ability to travel long distances on air and water currents, and their propensity to bio-accumulate in food chains. POPs will remain in the environment for a long time even if all new sources will be immediately eliminated as the rate of their degradation is very low. There is evidence that a lot of people worldwide may now carry enough POPs in their body fat to cause serious health problems, including reproductive and developmental problems, cancer, endocrine and immune system disruption, abnormal behaviour, and neurological problems. Twelve POPs have been identified by the United Nations Environment Programme (UNEP) as requiring urgent regulatory attention. They include the organochlorine pesticides (OCPs) aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, HCH, mirex and toxaphene. The remaining three POPs include polychlorinated biphenyls (PCBs), dioxins and furans[1]. Even though the use and production of OCPs have been regulated worldwide, in agreement with the Stockholm convention in 2001[2], they are still posing serious environmental threat both to wildlife and humans[3]. Milk occupies an important place particularly in the diet of infants, children and plays a pivotal role in their growth and development. Being a fat rich food it is an important source of OCP accumulation and hence one of the convenient food stuff for measuring the persistent OCPs. In this contribution the distribution of OCPs in cow's milk samples collected from different sites in El-

Qalubiya governorate, Egypt were investigated.

MATERIALS AND METHODS

All the solvents used in the present study were pesticide residue grade (Alliance Bio, USA). The mixture of OCPs analytical standard was purchased from Dr. Ehrenstorfer, Augsburg, Germany. One hundred fresh milk samples (about 500 ml each) were collected from March to April, 2011 during milking hours i.e., early morning and evening in the pre-cleaned, oven dried, hexanes rinsed glass stoppered bottles of 500 ml capacity and were temporarily stored in refrigerator until analysis. Samples were collected from five districts of El-Qalubiya Governorate, Egypt, namely Benha, Kaha, Shebin El-Kanater, Tokh and Kafr Shokr. The samples were extracted according to the method described by Suzuki et al.[4]. Milk sample (10 ml) was measured into centrifuge tube and 20ml n-hexane, 5ml acetonitrile and 1 ml ethanol were added. The mixture was shacked vigorously for 1 min, and centrifuged at 2000 rpm for 2 min. The n-hexane layer was filtered through anhydrous sodium sulfate into 100 ml round bottom flask. The sample was re-extracted twice with 20 ml portion of n-hexane. The combined n-hexane phase was concentrated to about 4 ml using rotary evaporator. Milk extract was purified by Florisil minicolumn and OCPs were eluted from the column with 50 ml ethyl acetate-benzene-n-hexane (1 + 19 + 180). The elution was concentrated using a rotary evaporator to dryness. The residue was dissolved in 2 ml of n-hexane and transferred into autosampler vial for GC-ECD analysis. Analysis was carried out on an Agilent 7890, gas chromatograph, equipped with electron capture detector (GC-ECD). GC analysis was conducted on a HP-5MS capillary column of 30 m, 0.25 mm id., 0.25 µm film thickness. The oven temperature was programmed from an initial temperature 160 (2 min hold) to 260 ºC at a rate of 5º C min-1 and was maintained at 260 ºC for 12 min. Injector and detector temperature were maintained at 300 and 320 ºC, respectively. Nitrogen was used as a carrier at flow rate of 3 ml min-1. With each set of samples to be analyzed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. Method sensitivity and recovery were determined by using samples spiked with the tested pesticides at three levels. At each fortification level three replicate were made. Fortified samples were extracted as described earlier and the average recovery percentages of OCPs for fortified samples were determined and calculated for all tested compounds in milk (TABLE 1).

Data were statistically evaluated by one-way analysis of variance (ANOVA). Determination the differences among means were carried out by using the least significant differences (LSD) test. All statistical analysis was done using the statistical package for social sciences (SPSS 16.0) program.

TABLE 1 : Percent recovery from fortified milk samples and the minimum detection limits (ng g^{-1}) for various pesticides.

Pesticide Name	Recovery	RSD	LOD
γ-HCH	93	9	0.01
δ-HCH	95	5	0.04
Aldrin	92	8	0.01
Endrin	96	3	0.01
Dieldrin	102	6	0.02
Heptachlor	98	10	0.03
Hept. Epoxide	100	8	0.03
γ-chlordane	91	6	0.02
Endosulfane	94	12	0.02
p,p'-DDE	98	5	0.05
p,p'-DDD	95	7	0.05
p,p'-DDT	99	10	0.05

RESULTS AND DISCUSSION

OCPs are among the most important organotoxins and make a large group of pesticides. They are classified into three groups: hexachlorocyclohexane isomers (HCHs), cyclodienes (aldrin, endrin dieldrin, heptachlor, heptachlor epoxide, γ-chlordane and endosulfane) and DDT and its metabolites (DDT, DDE, DDD). Physicochemical properties of these toxins, especially their high lipophylicity, facilitate the absorption and storage of these toxins in human and animal bodies. The existence of the residues of these toxins in milk which is one of the most widely used foodstuff containing lipids can be a quantitative and qualitative index for the presence of these toxins in animal bodies. Out of all the samples analyzed, 12 OCPs residues were detected. These were: δ-HCH, aldrin, dieldrin, heptachlor epoxide, γ-chlordane, endosulfane, endrin, p,p'-DDE, p,p'-DDD, p,p'-DDT. The range, mean and frequency of the OCPs residues detected are presented in TABLE 2. The residue levels are expressed in ng/ml milk without correcting for percent recoveries. All samples were contaminated with one or more of the investigated pesticides. The major OCPs residues found in the cow's milk were p,p'-DDD (49%) and endrin (42%).

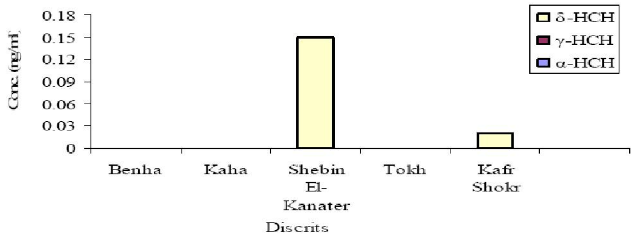

Figure 1 : Residues of HCH isomers in cow's milk from El-Qalubiya Governorate.

Aldrin, dieldrin, heptachlor epoxide, γ-chlordane, endosulfane, p,p'-DDE and p,p'-DDT were present in 30%, 35%, 29%, 13%, 12%, 12% and 6 % with a mean value of 0.382, 3.983, 1.810, 1.034, 0.619, 0.347 and 5.043 ng/ml, respectively in cow's milk samples, whereas α-HCH, γ-HCH and heptachlor were not detected in any of the analyzed samples. The district wise concentrations of different pesticide are given in Figure 1, 2and 3. The maximum concentration of δ-HCH, dieldrin, p,p'-DDT and "OCPs was found in cow's milk samples from Shebin El-Kanater, Kaha, Benha and Kaha district, respectively. Among HCH isomers, δ-HCH was only found in cow's milk samples. Among "DDT, p,p'-DDD contributed more as compared to other metabolites. The δ-HCH was found in 2% of cow milk samples with concentration varied from below the detection limit (BDL) (>0.04 ng/ml) to 0.15 ng/ml with a mean value of 0.085 ng/ml. The p,p'-DDD contributed to 49% (0.513 ng/ml) followed by p,p'-DDE 12% (0.347 ng/ml) and p,p'-DDT 6% (5.043 ng/ml) (Figure 3). The presence of p,p'-DDD and p,p'-DDE indicates mainly past exposure to this insecticide. The high proportion of p,p'-DDD in milk has been ascribed to reductive dechlorination of p,p'-DDT by rumen microorganisms[5].

OCPs persist in the environment after they are used and are translocated and biomagnified along the natural food chains, with possible deleterious effects on organisms placed at higher tropic levels. For example, hyporeflexia in infants has been associated with DDE

TABLE 2 : Residues of organochlorine pesticides (ng/ml) raw cow's milk from El-Qalubiya Governorate.

Pesticide Name	Range	Mean ±S.D (n = 100)	No. of +ve samples
α-HCH	BDL	-	-
γ-HCH	BDL	-	-
δ-HCH	BDL-0.15	0.085± 0.091	2
E-HCL	BDL-0.15	0.085±0.091	2
Aldrin	BDL-3.80	0.382±0.749	30
Endrin	BDL-3.20	0.457±0.566	42
Dieldrin	BDL-33.0	3.983±8.114	35
Heptachlor	BDL	-	-
Heptachlor Epoxide	BDL-6.20	1.810±1.412	29
γ-chlordane	BDL-2.80	1.034±0.944	13
Endosulfane	BDL-5.20	0.619±1.466	12
p,p'-DDE	BDL-1.14	0.347±0.377	12
p,p'-DDD	BDL-6.16	0.513±1.041	49
p,p'-DDT	BDL-20.8	5.043±7.863	6
E-DDT	BDL-20.8	0.920±2.777	67

BDL: below the detection limit

levels as low as 4 mg/kg milk fat in breast milk[6], DDT causes egg-shell thinning in some birds[7], aldrin and dieldrin are potentially carcinogenic[8], and lindane produce liver tumors in mice[8]. Aldrin was detected in 30% of milk samples collected with concentration varying from >0.01 to 3.80 ng/ml, with a mean concentration value of 0.382±0.749 ng/ml. Endosulfane and γ-chlordane were detected in only 12% and 13% samples with concentration varying from >0.02 to 5.20 ng/ml and >0.02 to 2.80 ng/ml, respectively.

There are number of reports available about the occurrence of OCPs residues in milk from different parts of Egypt as well as abroad although it has been found that there is a steady decline in the level of those residues in milk and other products during recent years as a result of banning or restricting some of the compounds

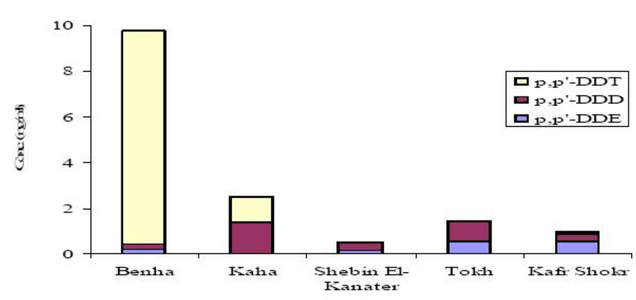

Figure 2 : Residues of DDT and its metabolites in cow's milk from El-Qalubiya Governorate.

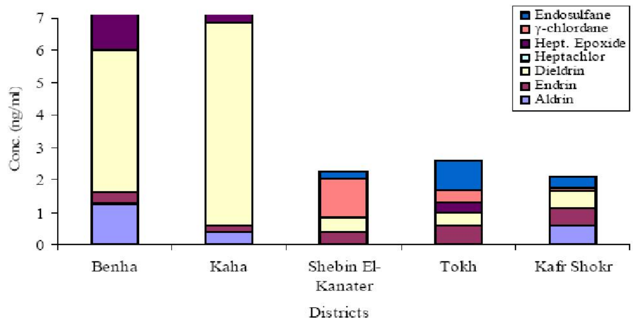

Figure 3 : Residues of cyclodiens pesticide in cow's milk from El-Qalubiya Governorate.

belonging to the group, introduction of newer molecules and changes in the management practices of insect pests, etc.

CONCLUSIONS

The presence and concentration of OCP residues in milk in the context of present study indicate that through the frequency and level has considerably decreased over the past records of particularly Egypt but still the exists albeit in low scale. The most important reason for this could be that most of the OCP have become the persistent environmental contaminants over the decade and have very less degradability. From public health point of view, the observed levels of OCPs residues in cow's milk's in this study do not pose a serious health risk to the consumers.

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