



Trade Science Inc.

ISSN : 0974-7419

Volume 11 Issue 5

Analytical CHEMISTRY

An Indian Journal

Full Paper

ACAIJ, 11(5) 2012 [176-179]

Organophosphorus pesticide residues in cow's milk from Egypt

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Received: 16th January, 2012 ; Accepted: 9th February, 2012

ABSTRACT

The concentrations of 12 organophosphorus Pesticides (OPPs), widely used in crops used for animal feed were determined in 100 samples of cow's milk collected from five districts of El-Qalubiya Governorate, Egypt during March to April, 2011. OPPs residues were measured by gas chromatography with a flame photometric detector. Approximately 8 % of the samples contained detectable levels of OPPs residues. Two samples contained residues exceeding established maximum residue limits (MRL), and the OPPs present in these samples were dichlorvos and chlorpyrifos. Samples containing more than one compound were not found. From public health point of view, the observed levels of OPPs residues in cow's milk's in this study do not pose a serious health risk to the consumers.

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KEYWORDS

Organophosphorus Pesticides;
Residues;
Cow's milk.

INTRODUCTION

Organophosphorus Pesticides (OPPs) are normally esters, amides, or thiol derivatives of phosphoric, phosphonic, phosphorothioic, or phosphonothioic acids. Most are only slightly soluble in water and have a high oil-to-water partition coefficient and low vapour pressure. They are generally among the most acutely toxic of all pesticides to vertebrate animals. They are also unstable and therefore break down relatively quickly in the environment^[8]. By the late 1970s, the use of OPPs began to over-take the organochlorine pesticides (OCPs) which included DDT. While OCPs were relatively safe to use, their problem was its persistence in the environment and detection in the human food chain. OPPs on the other hand are more acutely toxic, but, do not persist in the environment beyond a few months.

Agricultural use of pesticides can be expected to result in residues in food and feed. Since it is recognized that pesticides are needed to produce an economical food supply of high quality, the pesticide regulatory requirements are designed to ensure that the remaining residues do not constitute an unacceptable health risk.

During the last 50 years, the variety and usage of pesticides have increased in Egypt and worldwide. In Egypt there are no regular monitoring programmes concerning the identification and determination of different pollutants in the milk, although Egypt is the largest pesticide market in Arabian countries and the fourth largest importer of pesticides among developing countries. A few studies were carried out to measure the concentration of OCPs in milk. However, OPPs can become concentrated throughout the food chain. Cow's milk can absorb these compounds by all routes (inhalation,

ingestion and dermal absorption) and thus can secrete contaminated milk. This is favored by possible OPPs interactions with lipids and proteins. OPPs can appear in milk due to several possible causes: (a) use of insecticides directly on dairy cattle for ectoparasite control; (b) pasture, forages, or animal feed manufactured from plant material that has been treated with insecticides; and (c) use of insecticides in stables or dairy factories^[9]. The aim of this work was to study the possible presence in milk of the most commonly used OPPs implicated in milk production in our country.

MATERIALS AND METHODS

All the solvents used in the present study were pesticide residue grade (Alliance Bio, USA). The mixture of OPPs (dichlorvos, ethoprophos, cadusafos, diazinon, chlorpyrifos-methyl, pirimiphos-methyl, chlorpyrifos, parathion-methyl, pirimiphos-ethyl, malathion, prothiphos, profenophos) 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 Ministry of Welfare, Health and Cultural Affairs, Leidschendam, the Netherlands, multiresidue method 5 (submethod 3) for the analysis of organophosphorus compounds in milk was used^[2]. Milk (50 ml) was blended with ethyl acetate (100 ml). Sodium sulfate (50 g) was added, and the mixture was shaken and then allowed to stand for 2-3 min. The upper layer was decanted, and a 50 ml aliquot was evaporated to dryness in a rotating evaporator (35 °C). The residue was dissolved in hexane (10 ml) and then extracted with 2 x 25 ml of acetonitrile, saturated with hexane. Combined acetonitrile phases were evaporated to dryness, as described above. The residue was dissolved in 2 ml of ethyl acetate and transferred into autosampler vial for GC-*FPD* analysis. The same volume of solvents and anhydrous sodium sulfate, which used in extraction of OPPs from milk samples were

subjected to the same procedures as the examined samples to detect any possible traces of the studied pesticides and its value was subtracted from the results. A Hewlett-Packard 6890 GC system equipped with a flame photometric detector GC/*FPD* and a phosphorus filter (526 nm) was used. GC analysis was conducted on a PAS-1701 (Agilent, Folsom, CA) fused silica capillary column of 30 m length, 0.32 mm id., and 0.25 μ m film thicknesses. The oven temperature was programmed from an initial temperature 160 (2 min hold) to 210°C at a rate of 5°C min⁻¹ and was maintained at 210°C for 3 min and raised to 240°C at rate of 5°C min⁻¹ and was maintained at 240°C for 1 min and raised to 270°C at a rate of 20°C min⁻¹ and was maintained at 270°C for 10 min. Injector and detector temperature were maintained at 240 and 260°C, respectively. Nitrogen was used as a carrier at flow rate of 3 mL/min. The hydrogen and air flow rate were 75 and 100 mL/min, respectively. Peak was identified by comparison of sample retention time value with those of the corresponding of pure standard compounds. Method sensitivity and recovery were determined by using samples spiked with the tested pesticides. Before analysis, relevant standards were run to check column performance, peak height, resolution, and limits of detection. With each set of samples to be analysed, a solvent blank, a standard mixture and a procedural blank were run in sequence to check for contamination, peak identification and quantification. The average recovery per-

TABLE 1 : Recovery percentage, relative standard deviation, method detection limits and maximum residue limits (mg/kg) of organophosphorus pesticides

Pesticide Name	Recovery %	RSD	LOD
Dichlorvos	88	5	0.001
Ethoprophos	78	8	0.001
Cadusafos	92	10	0.005
Diazinon	85	7	0.001
Chlorpyrifos-methyl	96	11	0.001
Pirimiphos-methyl	82	9	0.002
Chlorpyrifos	80	4	0.001
Parathion-methyl	91	8	0.001
Pirimiphos-ethyl	89	8	0.002
Malathion	96	13	0.001
Prothiphos	91	7	0.002
Profenophos	82	10	0.001

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centages of OPPs for fortified samples at different levels were determined and calculated for all tested compounds in each aquatic system compartment (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.

RESULTS AND DISCUSSION

OPP are so widely used because of their effectiveness against a wide variety of insects and their lack of persistence in the environment (compared to OCPs). Most of the OPPs are rapidly absorbed by all routes. This group of pesticides which act as potent cholinesterase inhibitors, generally have lower persistence and bioaccumulation compared with organochlorines, but are regarded as highly toxic^[12]. Their propensity for relatively short persistence, due to chemical and biological degradation, favours their usage. Although many OP pesticides are short-lived or are metabolized by the animals that ingest them, some are persistent and when applied in large amounts pervade the environment.

Dichlorvos, chlorpyrifos methyl and chlorpyrifos were detected in milk samples TABLE (2). The number of samples exceeding the MRLs established was two milk samples. Samples containing more than one compound were not found. The OPPs present in violative levels were dichlorvos (0.008-0.05 mg/kg) and Chlorpyrifos (0.001-0.096 mg/kg). The presence of dichlorvos may be explained due to their use as ectoparasiticides in dairy cattle. Dichlorvos is also used for insect control in brans and silos. The presences of dichlorvos residues in raw milk have been observed by^[9]. Chlorpyrifos methyl and chlorpyrifos may be present in milk because of their use in crops destined for animal feed such as alfalfa, sorghum, soy, and maize. Chlorpyrifos is one of the OPPs with higher use in our country. The presence of these OPPs contrast with the opinion of^[3], who considered that metabolic breakdown of OPPs is rather quick and that there is only a rare chance to observe their residues in milk. It is well-known that OPPs are less stable and persistent than OCPs;

however, there are several reports of their presence in cow's milk^[1,4,6,7,10,13]. Residues of diazinon, chlorpyrifos, and malathion in levels of 0.005-0.586 mg/kg^[5,11], 0.059 mg/kg^[4] and 0.110 mg/kg, respectively, have been reported. In addition to the moderate stability of OPPs, the very limited contamination measured in Egyptian raw milk could reflect the correct compliance with withdrawal times for plant protection products and/or veterinarian drugs and the observance of good farming and breeding practices.

TABLE 2 : Concentration (mg kg⁻¹) of organophosphorus pesticides in milk samples

Pesticide Name	Positive samples	Residue level rang (mg/kg)	Residue mean (mg/kg)	MRL (mg/kg)
Dichlorvos	2	0.008-0.05	0.029	0.02
Ethoprophos	-	-	-	-
Cadusafos	-	-	-	-
Diazinon	-	-	-	0.02
Chlorpyrifos-methyl	3	0.002-0.009	0.004	0.01
Pririmiphos-methyl	-	-	-	0.05
Chlorpyrifos	3	0.001-0.096	0.004	0.01
Parathion-methyl	-	-	-	-
Pririmiphos-ethyl	-	-	-	-
Malathion	-	-	-	-
Prothiphos	-	-	-	-
Profenophos	-	-	-	-

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