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Studies on organochlorine pesticide residues in butter in Punjab

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Abstract

The present study was conducted to investigate the magnitude of contamination of butter with pesticide residues in Punjab. Organochlorine pesticide residues were analyzed in twenty eight samples of commercially available butter brands and of home made butter collected from various parts of Punjab. The estimation was carried out by using multi residue analytical technique employing GC-ECD. All the samples of butter showed detectable residues of one or more organochlorine pesticides such as DDT, HCH, endosulphan and aldrin. The range of levels of ΣHCH residues was 0.092- 0.645 mg kg^{-1}. Mean α, β- and γ- and δ- HCH residue concentration in butter was 0.098, 0.048, 0.196 and 0.01 mg kg^{-1}, respectively. The range of levels of Σ DDT residues in butter was BDL - 0.469 mg kg^{-1}. Mean concentration of p,p' ΣDDD, p,p'-DDE and p,p'-DDT was 0.142, 0.114 and 0.022 mg kg^{-1} respectively. All samples of butter had ΣDDT residues below MRL of 1.25 ppm but 53 per cent butter samples had gamma-HCH residues more that MRL of 0.2 ppm as prescribed by PFA in India.

Keywords: butter, DDT, endosulphan, HCH, pesticide residues.

Introduction

The indiscriminate use of organochlorine pesticides (OCP's) with poor enforcement of regulations and their persistent nature have contributed to the prevalence of residues of these pesticides in food commodities in India (Mukherjee and Gopal, 1993; Battu *et al.*, 1996; Adiroubane and Letchoumanae, 1999; Kalra *et al.,* 1999; Bedi *et al.,* 2004). Milk and milk products are the major sources of dietary exposure to DDT and HCH in human beings in India (Kannan *et al.*, 1997). Organochlorine pesticide residues in milk and milk products like butter, ghee and cheese have been viewed with great concern as these are important part of Indian diet and have been reported by various workers (Dhaliwal and Kalra, 1978; Kumari and Kathpal, 1995; Battu *et al.*, 2004; Kumar *et al.*, 2005). Organochlorine pesticides are lipophilic in nature so during processing of milk to butter these pesticides are transferred and magnified in butter. Therefore, present study was undertaken to ascertain the levels of contamination of butter with organochlorine pesticide residues in Punjab.

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Materials and Methods

Twenty eight samples of butter, each sample weighing between 100-250 g, depending upon the pouch size of commercially available popular butter brands and of home made butter were collected from various parts of Punjab. The samples were kept refrigerated until analysis.

All the chemicals of Analytical Reagent (AR) quality were obtained from E Merck (India) Ltd and the solvents were glass distilled before use. The suitability of the reagents/solvents was checked by running blanks. Butter sample was heated to 60°C in a water bath and fat was separated and a representative 5 g sample of melted butter was dissolved in 40 ml hexane and partitioned three times with equal volumes of saturated acetonitrile with hexane. Acetronitrile fractions were combined and diluted 4-5 times with 10% NaCl solution partitioned thrice with hexane, followed by partitioning thrice with dichloromethane. Hexane and dichloromethane fractions were combined and concentrated to near dryness on rotary vacuum flash evaporator. The residues were redissolved in acetone and transferred into 10 ml centrifuge tubes for further estimation using gas liquid chromatograph (GLC).

The residues in cleaned up extracts were

quantified using Gas Liquid Chromatography (GLC). The Electron Capture Detector (ECD) was used for organochlorine. Instrumental parameters and operating conditions were as follows:

Gas Chromatograph	: Nucon 5700
Detector	: ECD, Ni 63
Columns	: o.d. 1/8", i.d.3 mm, L - 4",
Support	: Chromosorb W.H.P.
Liquid phase	: 1.5% OV-17+1.95% OV-210
Temperatures	:
Injection port	: 230°C
Column	: 220°C
Detector	: 260°C

The cleaned up extract measuring 2-8ug was injected in GLC. Winacid 5.1 software on PC was used for integration and computation of signals. The compounds were identified and quantified by comparison of the retention time and peak heights/ area of the sample chromatographs with those of standards run under the same operating conditions. The standards were run before and after all p,p'-DDT analyses. The results were confirmed by using alternate columns. The percent recoveries were in the range of 85-92 when spiked with 0.10 mg kg^{-1} for p, p'-DDT and lindane.

Results and Discussion

In the present study all the samples of butter showed detectable residues of one or more organochlorine pesticides. Residues of Σ DDT (p,p'- DDD, p,p'-DDE and p,p'-DDT), HCH (α-, β- and γ- and δ- HCH), Σ endosulphan (p,p'-DDT endosulphan A and endosulphan sulphate) and dieldrin were recorded in butter samples. Mean Σ HCH residues concentration was found to be 0.352 mg kg^{-1} for butter with range of 0.092- 0.645 mg kg^{-1}. Mean α-, β- and γ- and δ- HCH residue concentrations in butter were 0.098, 0.048, 0.196 and 0.01 mg kg^{-1}, respectively (Fig.1). In butter γ-HCH was major component of Σ HCH i.e. 55 per cent followed by α-HCH (28%), β-HCH (14%) and δ-HCH (3%). Mean Σ DDT residues levels in butter were 0.278 mg kg^{-1} with range of BDL - 0.469 mg kg^{-1}. Mean concentration of p,p' p,p'-DDT, DDD, p,p'-DDE and p,p'-DDT were 0.142, 0.114 and 0.022 mg kg^{-1}, respectively, (Fig.2) and proportion in Σ DDT were 51, 41 and 8 per cent, respectively. Mean Σ endosulphan residues were 0.023 mg kg^{-1} and range was BDL-0.212 mg kg^{-1}. Mean dieldrin residue was 0.003 mg kg^{-1} and range was BDL-.016 mg kg^{-1}

The organochlorine insecticides persist for a long time in the environment and appear even decades after their use in soil and environment (Nerin *et al.*, 1996; Harner *et al.*, 1999) and contaminate animal feed and fodder. The presence of HCH, DDT and other pesticides in fodder, concentrate feed and roughage have been reported by various workers (Dethe *et al.*, 1996; Singh *et al.*, 1997; Gill *et al.*, 2001) that could be the main source of organochlorine contamination of dairy milk samples. In India about 44.5% of the total pesticides consumption is for cotton crop (Agnihotri, 1999) which may lead to accumulation of residues in cotton seeds which are regularly fed to milch animals. The residues of OCP's have the capability of bioaccumulating and transferring to milk through the animal's body, from its feed, from topical application for ectoparasites, and from the air they breathe. Due to lipophillic nature of OCP's, they are stored in fat rich tissues of animal and subsequently translocated and excreted through milk which further accumulate in fat rich dairy products such as butter, ghee and ultimately consumers of dairy products are exposed to these residues (Kanan *et al.*, 1992; Waliszewaski *et al.*, 1997). Smart *et al.* (1972) observed that lactating cows fed 0.05 ppm aldrin, 0.2 ppm γ-HCH and 2.0 ppm p,p'-DDT in their concentrate ration gave detectable residues of dieldrin, γ-HCH, *pp*'-DDE, p,p'-TDE and p,p' -DDT in the milk and also aldrin in the butter and cheese even after 28 days of feeding.

The most of earlier reports from India and abroad (Dhaliwal and Kalra, 1978; Kalra *et al.*, 1983; Lata *et al.*, 1984; Kannan *et al.*, 1992) have shown high concentration of various OCP's residues in butter. The studies conducted in Gujrat, Haryana and Andhra Pradesh during 1989-92 showed presence of DDT metabolites ranging from 0.01-5.84 ppm and HCH isomers ranging from

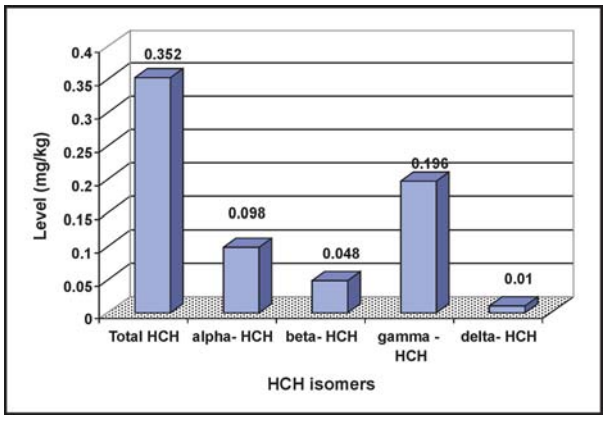


Fig.1: Levels of HCH isomers in Butter

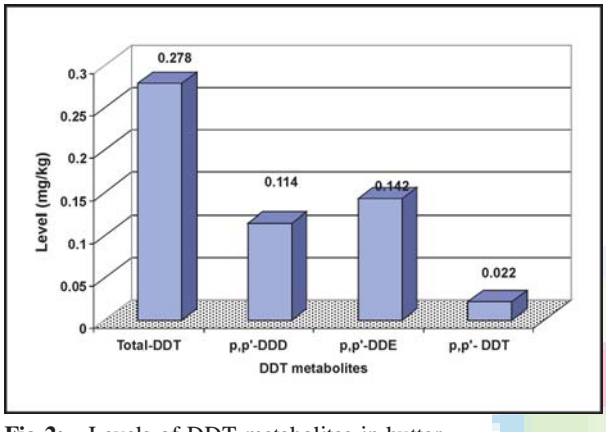


Fig.2: Levels of DDT metabolites in butter

0.22 to 5.80 ppm (Narsimha Rao *et al.*, 1989, Shah *et al.*,1992, Kathpal *et al.*,1992). Kalra *et al.* (1983) reported levels of Traces-16.04 ppm and 0.02-11.97 ppm for DDT and HCH, respectively, in butter samples collected from all over India. But in present study levels are much less than the earlier reports. The possible reason of relatively less residues of HCH and DDT can be attributed to restricted use/ban of these insecticides in agriculture in India during the last one decade.

The substantial change in the isomeric composition of HCH in butter was found in the present study as compared to earlier reports. Levels of γ-HCH residues were highest followed by α- HCH whereas levels of β- and δ- HCH were very less. Earlier reports also showed high concentration of α- and β-HCH but less concentration of γ-HCH. In the present study the proportions of various HCH isomers in market milk were α-HCH (28%), β-HCH (14%), γ-HCH (55%) and δ-HCH (3%). Recent reports also showed high residues of γ-HCH as major HCH isomer (Fayed *et al.*, 1993; Waliszewski *et al.*, 1996; Battu *et al.*, 2004). The change in the pattern of HCH residues can be due to ban imposed on use of technical HCH w.e.f. 1.4.1997 and only γ-HCH can be used for field application on crops. Among various HCH isomers only γ- HCH has the insecticidal property and is the only isomer of HCH which is permitted for use in agriculture. The presence of residues of p,p'-DDT metabolite in butter in present study, indicated the recent use of DDT, which may be during vector control operations.

All samples of butter had Σ DDT residues below MRL of 1.25 ppm but 53% butter samples had γ-HCH residues more that MRL of 0.2 ppm as prescribed by PFA in India.

Presence of residues of DDT and HCH in milk products is a matter of concern and it indicates that these OCP's still persists in our environment even after their restricted use/ban in agricultural and public sectors. Use of technical HCH has been completely banned and use of DDT is restricted to public health programmes. Residues are still encountered in human and bovine milk and it takes many years for substantial decrease in residues levels. However there is need of continuous monitoring of milk, milk products and human load so as to know exact status of contamination in different matrices to ensure safety to consumers and guidelines for policy makers. Contamination of environment, livestock and food of animal origin can be avoided by better management and judicious use of pesticides adopting Integrated Pest Management (IPM), banning of persistent organochlorine pesticides with strict compliance and bringing more awareness about residues among public and farmers.

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