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Level of organochlorine pesticide residues in dry fruit nuts

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Abstract: *The use of pesticides on cash crops and exportable food commodities had always been a serious concern. Fruits form one of the important constituents of human diet, in that they give one third of the requirement of calories, vitamins, and minerals. This study has been carried out to determine the level of organochlorine pesticides namely HCH, DDT and Endosulfan in raw fruit nuts. Nuts have proteins and high level of fat content. These properties of nuts attract organochlorine pesticides to accumulate. The analysis of organochlorine pesticide residues in commonly used dry fruits like Cashew nut, Walnut, Coconut , Chilgoza , Chironji, Makhana, Resins, Apricot, Almonds, Date palm , Pistachio nut collected from local market of Lucknow. India has indicated presence of very low level of HCH (0.007-1.328 mg kg^{-1}), DDT (ND-0.140 mg kg^{-1}) and Endosulfan (ND-0.091 mg kg^{-1}).There are no MRL values established for nuts in the country. This finding is based on a smaller number of samples, which however suggest that the presence of low level of DDT, HCH and Endosulfan might be due to environmental rather than direct exposure.*

Key words: *Organochlorine pesticides, Residues, Fruit nuts*
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Introduction

Pesticides are the chemicals used for the control of pest infestation to the crops. However the extensive use of pesticides may result into their accumulation in the agriculture produce. Their low biodegradability has classified these chemicals as persistent toxic substances (UNEP, 2002). It is in this context that pesticides in general and total DDT (dichlorodiphenyltrichloroethane), hexachlorocyclohexane (HCH), endosulfan, aldrins, dieldrin, heptachlor, chlordane and other related compounds in particular play important role in contamination of the environment, causing ecological impacts (Oxynos *et al*., 1989). These organochlorine pesticides have a wide range of acute (Dikshith *et al*.,1989) and chronic health effects (Dikshith *et al*., 1991), including neurological damage (Raizada *et al*.,1993) and developmental effects (Srivastava and Raizada, 2000) in animals. Many organochlorine pesticides are also suspected endocrine disruptors (WHO, 1990; Raizada and Dikshith, 1991; EPA, 1997). Humans exposed occupationally are also at risk, and there are studies linking exposure at work to reduce sperm counts, increased time to pregnancy and increased rate of birth defects in offspring (Colborn, 1998). High chemical, biological stability and higher degree of lipophilicity results into their accumulation in biological tissues and food commodities (Wania and Mackay, 1996) and environmental components (Seth *et al*., 1998).

Fruits form one of the important constituents of human diet, in that they give one third of the requirement of calories, vitamins and minerals. In addition, increased cultivation and consumption of fruits require less land per capita and their production can give more nutrients per acre than other foods. The dried seeds of nuts are eaten as raw, roasted, pureed or used as flour. Nuts are the best source of protein, fats and vitamin E. They contain cholesterol-free unsaturated fats, magnesium, chromium, zinc and manganese. Different types of nut are being consumed in large scale in northern part of the country.

The use of pesticides on cash crops and exportable food commodities had always been a serious concern. Further lack of information on the presence of pesticide residues in dry fruits has also affected its export. The present study deals with the analysis of organochlorine pesticide residues in commonly used dry fruits nuts like Cashew nut (*Anacardium occidentale*), Walnut (*Juglans niger*), Coconut (*Cocos nucifera*), Chilgoza (*Pinus gerardiana*), Chironji (*Buchania lanzan*), Makhana (*Euryale ferox*), Resins (*Vitis vinifera*), Apricot (*Prunus armeniaca*), Almonds (*Prunus amygdalus*), Date palm (*Phoenix dactylifera*) and Pistachio nut (*Pistachio vera*) .

Materials and Methods

All the solvents used in extraction and clean up process were of HPLC grade procured from E. Merck India limited. The dry fruit samples (Cashew nut, Walnut, Coconut, Chilgoza, Chironji, Makhana, Resins, Apricot, Almonds, Date palm and Pistachio nut) were collected from local Lucknow market and analyzed as per the standard procedure of AOAC (2005). 3 gm of each dry fruit in triplicate was grinded, taken in 20 ml test tube containing 15 ml petroleum ether. Test tubes were mixed thoroughly and shaken on mechanical shaker for 10 minutes. The extracts obtained after passing the sample through a filter paper transferred to separatory funnel for liquid-liquid partition. If color present in the samples, it was removed by cleanup. It was passed through a glass column (25 cm x 10 mm i.d.) packed with charcoal and silica gel. Extract after cleanup was evaporated till dryness and final makeup done with n-Hexane.

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Aliquots of above concentrate were injected to pre calibrated GC machine (Nucon 5765) equipped with ^{63}Ni electron capture detector. A glass column (1.5 m x 2 mm id) packed with 1.5% OV-17 + 1.95% QF-1 on 100-120 mesh chromosorb WHP was used. Operation temperatures were programmed at 195, 200 and 220°C for column, injector and detector, respectively. Purified nitrogen gas, passing through silica gel and molecular sieves was used as carrier gas at flow rate 60 ml min^{-1}. Periodical procedural blanks were used to check cross contamination. Recovery studies with purified samples indicated that overall recovery value exceeded 85%. Identification and quantification of DDT and its metabolites, HCH and its isomers and endosulfan were accomplished using known amount of external standards, received from USEPA, pesticides and industrial chemicals repository (MD-8) Research triangle, NC, USA.

Results and Discussion

The residues of different isomers and total HCH detected in dry fruits are shown in Table 1.The residues of total HCH was found maximum (1.328 mg kg^{-1}) in Chironji and minimum in Apricot, Resins and Makhana (0.007 mg kg^{-1}). In rest of the dry fruits the residues was below 0.2 mg kg^{-1}. The residues of *pp´* -DDE, *op´* -DDT, *pp´* -DDT, *op´* -DDD and total DDT are shown in Table 2. The residues of total DDT found below 0.1 mg kg^{-1} in all the nuts analyzed except Cashew nut (0.140 mg kg^{-1}). Residues of DDT were absent in Resins. The residues of endosulfan in different nuts are shown in Table 3. Endosulfan was found at 0.091 mg kg^{-1} level (highest) in cashew nut and lowest in date palm (0.004 mg kg^{-1}). Makhana did not contain residues of endosulfan. Subramanian *et al.* (2007) have reported the residues of total HCH and total DDT as 0.62 and 0.21 mg g^{-1} wet weights, respectively, in Cashew nut from Chennai, India.

Organochlorine pesticides and fumigants were analysed in nut samples from UK during 1994 and 2000. Methyl bromide was found present in 49% of the samples. According to Pesticide Residues Monitoring Report inorganic bromide was the most frequently found compound as expected, because the nuts are being fumigated before transportation and processing. Chlordane, DDT, endrin, alpha, beta, gamma-HCH, heptachlor, hexachlorobenzene and hydrogen phosphide were actively sought but not found at or above their reporting limits *(i.e.* 0.01 mg kg^{-1} for all the pesticides and 0.001 mg kg^{-1} for hydrogen phosphide). There are no reports available in India on the pesticide residues in nuts.

Table - 1: Values (n=3) of total HCH and different isomers (mg kg^{-1}) in dry fruit nuts*

Dry fruits	Alpha	Beta	Gamma	Delta	Total HCH
Cashew nut	0.053	0.036	0.007	0.027	0.123
Walnut	0.118	0.014	0.004	0.038	0.166
Almond	0.028	0.007	0.008	0.030	0.073
Pistachio nut	0.112	0.013	0.015	0.013	0.153
Coconut	0.054	0.012	0.005	0.028	0.099
Chilgoza	0.074	0.008	0.004	0.020	0.106
Chironji	0.050	0.001	1.260	0.017	1.328
Apricot	0.003	0.002	0.002	ND	0.007
Date palm	0.008	0.015	0.002	0.002	0.027
Resins	0.002	0.002	0.003	ND	0.007
Makhana	0.001	0.004	0.001	0.001	0.007

Values < 0.001 mg kg^{-1} = ND, * = Netherlands MRL values 0.1 mg kg^{-1}

Table - 2: Values (n=3) of total DDT and different metabolites (mg kg^{-1}) in dry fruit nuts

Dry fruits	*pp´* DDE	*op´* DDT	*op´* DDD	*pp´* DDT	Total DDT
Cashew nut	0.004	0.136	ND	ND	0.140
Walnut	ND	0.045	ND	ND	0.045
Almond	0.004	ND	ND	ND	0.004
Pistachio nut	0.021	ND	ND	0.001	0.022
Coconut	ND	0.044	0.002	0.001	0.047
Chilgoza	0.009	ND	0.032	ND	0.041
Chironji	0.001	ND	ND	ND	0.001
Apricot	0.033	0.003	ND	ND	0.036
Date palm	0.004	0.003	ND	ND	0.007
Resins	ND	ND	ND	ND	ND
Makhana	ND	0.001	ND	0.001	0.002

Values < 0.001 mg kg^{-1} = ND, * = Netherlands MRL values 0.1 mg kg^{-1}

Table - 3: Values (n=3) of endosulfan (mg kg^{-1}) in dry fruit nuts

Dry fruits	Endosulfan
Cashew nut*	0.091
Walnut*	0.021
Almond*	0.032
Pistachio nut*	0.014
Coconut*	0.017
Chilgoza	0.034
Chironji	0.079
Apricot	0.037
Date palm	0.004
Resins**	0.011
Makhana	ND

Values < 0.001 mg kg^{-1} = ND, *Dutch MRL values 0.1 mg kg^{-1}, ** 2.17 mg kg^{-1}

Consumer products *i.e.* tea and coffee have been analyzed for DDT and HCH residues. Though MRL values have not been fixed, however the levels recorded were thought to be not high enough (average 0.234 mg kg^{-1} for HCH in filter coffee) to suggest any adverse effects (Seth *et al*., 1998). Spices the most highly valued exportable commodities were also studied in India for residues of organochlorine pesticides. The results of which have indicated presence of DDT and HCH below 0.05 mg kg^{-1} (Srivastava *et al*., 2001). Similarly, very low level of HCH and DDT have been reported in herbal preparations (Srivastava *et al.*, 2000,2006). There is no MRL/tolerance limit of organochlorine pesticides in nuts in the country prescribed by PFA (1954), however HCH at 1.328 mg kg^{-1} in Chironji, DDT at 0.140 mg kg^{-1} and endosulfan at 0.091 mg kg^{-1} in Cashew nut appears not enough to cause adverse health effects. Though the number of samples analyzed for pesticide residues in nuts (products containing high fat content) being very few, the study has given some indication for the presence of residues and desires for more data. In general, milk and milk products, edible oils and fruits have higher levels of pesticide residues (Pandit, 2002; Dikshith *et al.*, 1989; Nath, 2003). Because of growing concern that the pesticides in general may gradually lead to toxicity (Ecobichon, 2001) and environmental contamination (Seth *et al*., 1998; ILSI, 2003), the Government has banned the use of HCH, and restricted the use of DDT in the country. The presence of even low level of DDT, HCH and endosulfan in fruit nuts may be due to environmental rather than direct exposure.

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