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Organochlorine Pesticide Residues in Indian Spices

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The use of plant materials for preparations of medicines and spices for taste and flavour has been known since ancient periods (Ensminger et al 1994). Spices are at a great demand in India and various other countries and therefore being exported from India. The use of organochlorine pesticides (OCPs) in developing countries has been of serious concern because of their persistant nature. The presence of OCPs in terrestrial and aquatic environment may lead to toxicological implications (Aruda et al. 1988, Cochieri and Arnese 1988, Sarkar and Gupta 1988, Dikshith et al. 1989). Pesticides in large amount are used in agriculture sector and public health programmes every year (Pesticide Manual 1997; Ciers 1998). Continuous use of OCPs lead to their presence in water, soil, air, crop plants and biological tissues. In addition to the direct consumption in food, spices used as drugs, tonics, toiletories, cosmetics etc. may contain OCP residues. Though, pesticide residue analysis have been done in several food/food products (Raizada et al. 1998). There is inadequate information on the presence of OCPs in various varieties of spices. The present study deals with the analysis of OCP residues in commonly used spices like cumin (*Cuminum cyminum*), chilli (*Capsicum frutescens*), dry ginger (*Zinger officinale*), carraway (*Carum ajwan*), ani seed (*Pimpinella anisum*), black pepper (*Piper nigrum*), fenugreek (*Trigonella foenum-graceum*), turmeric (*Curcuma longa*) and corriander (*Coriander sativum*) of the local market.

MATERIALS AND METHODS

All the solvents used in extraction and cleanup processes were of HPLC grade procured from M/s Spectrochem Pvt. Ltd. Bombay. Activated charcoal, sodium sulfate, sodium chloride and other

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chemicals, used in the study were procured from E. Merk India Ltd., BDH, and Glindia Ltd.

Samples of spices five each of dfferent brand were collected from local market of Lucknow for analysis. Analysis was carried out as per AOAC (1995). Each sample in triplicate 50g was taken in 500 ml conical flask mixed with 3x100ml (n-hexane : acetonitrile mixtrure 1:3), kept for over night and shaken for 30 min. After decanting organic phase was separated from aqueous phase and collected together. Aqueous phase was further extracted 3 times with 50 ml n-hexane in separatory funnel. Total pool of hexane extract was washed with distilled water 3 times. Washed hexane extract was further passed through charcoal and anhydrus sodium sulfate column. The clean hexane extract was concentrated and made 5 ml in a cleaned volumetric flask. Aliquotes of above concentrate were injected to precalibrated GC machine (Nucon 5765) equiped with ^{63} Ni electron capture detector. A glass column (1.5m x 2mm 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, 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 of 60 ml/min. Periodically procedural blanks were used to check cross contamination. Recovery studies with purified samples indicated that overall recovery value exceeded 80%. Identification and quantification were accomplished using known amount of external standered recieved from US EPA, Pesticides and Industrial Chemicals repository (MD-8) Research triangle, NC,USA.

RESULTS AND DISCUSSION

Results have shown that the level of HCH was more than the level of DDT in majority of the samples like cumin, chilli,dry ginger, carraway, aniseed black pepper, fenugreek, turmeric and corriander . The maximum value of total HCH was 0.203 ppm in turmeric and minimum 0.009 ppm in corriander (table.1) . The DDT level was maximum in fenugreek 0.086 ppm and minimum in dry ginger 0.005 ppm (table.2). The HCH isomers analysed revealed that beta HCH was found maximum in carraway ie. 0.162 ppm, whereas alpha HCH was maximum in chilli ie. 0.106 ppm. Maximum level of gamma HCH was in turmeric samples 0.117 ppm. Delta- isomer

Table 1. HCH isomers (ppm) in spices

SPICES	α-HCH	β-HCH	γ-HCH	δ-HCH	Total-HCH
Turmeric	0.033 (0.001-0.116)	0.007 (ND-0.024)	0.117 (0.004-0.232)	0.056 (ND-0.249)	0.203 (0.028-0.374)
Dry Ginger	0.016 (0.009-0.023)	0.012 (0.009-0.014)	0.069 (0.068-0.698)	Tr	0.097 (0.093-0.101)
Coriander	0.006 (ND-0.010)	0.001 (ND-0.001)	0.003 (ND-0.003)	Tr	0.009 (ND-0.010)
Cumin	0.014 (0.011-0.035)	0.003 (Tr-0.007)	0.013 (0.001-0.032)	0.017 (0.001-0.055)	0.0467 (0.028-0.060)
Aniseed	0.007 (0.003-0.01)	0.005 (ND-0.008)	0.007 (0.003-0.009)	0.006 (Tr-0.013)	0.018 (0.020-0.026)
Black pepper	0.002 (0.001-0.003)	0.015 (0.004-0.040)	0.019 (0.001-0.041)	0.021 (ND-0.054)	0.056 (0.013-0.070)
Carraway	0.016 (0.003-0.053)	0.162 (0.001-0.339)	0.007 (0.001-0.018)	0.010 (Tr-0.018)	0.196 (0.009-0.396)
Chilli	0.106 (0.001-0.378)	0.001 (Tr-0.001)	0.018 (ND-0.048)	0.022 (0.001-0.055)	0.145 (0.012-0.455)
Fenugreek	0.008 (Tr-0.028)	0.002 (0.001-0.004)	0.008 (0.002-0.025)	0.032 (0.001-079)	0.057 (0.006-0.232)

Detection limit 0.0001ppm. Values in parenthesis are the range. values rounded off to three places of decimal . Tr = values less than 0.001 ppm. ND = not detected.

Table 2. DDT and its metabolites (ppm) in spices

SPICES	pp'DDE	op'DDT	pp'DDD	pp'DDT	Total DDT
Turmeric	0.005 (ND-0.010)	0.013 (ND-0.030)	ND	0.033 (ND-0.124)	0.051 (ND-0.124)
Dry ginger	ND	ND	ND	0.005 (ND-0.005)	0.005 (ND-0.005)
Coriander	ND	0.078 (ND-0.078)	ND	0.003 (ND-0.003)	0.082 (ND-0.082)
Cumin	0.002 (Tr-0.003)	0.033 (0.004-0.057)	Tr	0.020 (0.001-0.038)	0.055 (0.001-0.091)
Aniseed	ND	0.023 (0.002-0.052	ND	0.023 (Tr-0.056)	0.045 (0.004-0.089
Black pepper	ND	0.018 (ND-0.040)	0.003 (ND-0.003)	0.005 (ND-0.012)	0.026 (ND-0.033)
Carraway	0.001 (ND-0.001	0.010 (ND-0.014	Tr	0.003 (ND-0.003	0.016 (ND-0.017)
Chilli	0.003 (ND-0.003)	0.010 (0.004-0.016)	ND	0.011 (Tr-038)	0.023 (0.001-0.045)
Fenugreek	Tr	0.018 (ND-0.050)	0.001 (ND-0.001)	0.067 (ND-0.297)	0.086 (0.002-0.297)

Detection limit 0.0001ppm. Values in parenthesis are the range. values rounded off to three places of decimal . Tr = values less than 0.001 ppm. ND = not detected.

of HCH was found in low concentration i.e. 0.056 ppm or less than this in all the samples . There is no MRL/Tolrance limit of organochlorine pesticides in spices prescribed in PFA (1954) or Codex (1996). However, Sullivan (1980) reported the total level of DDT and BHC below 0.5 ppm in spices imported into United States, and concluded that the levels of above pesticides in general are sufficiently low to be of no cause of alarm. Our studies have also shown low level 0.203 ppm (BHC) and 0.086 ppm (DDT) in spices. All the isomers of HCH were present in each sample of spices except in dry ginger and corriander. However, in case DDT samples have shown the presence of one , two or three metabolites of DDT . It is well known that organochlorine pesticides are lipophillic in nature and get accumulated in fat. An attempt has also been made to correlate the fat content as reported by Ensminger et al (1994) and the level of HCH and DDT in spices. It has been noted that accumulation of pesticides was not related to the fat content (table 3).

Table 3. Ratio of HCH and DDT among fat content in spices

SPICES	Spice (g) in 1 tsf	Fat (g) in 1 tsf spice	HCH (ug) in 1 tsf spice	DDT (ug) in 1 tsf spice	HCH ug/g fat	DDT ug/g fat
Turmeric	2.2	0.22	0.457	0.11	2.07	0.51
Dry ginger	1.8	0.11	0.174	0.01	1.58	0.07
Corriander	1.8	0.32	0.015	0.15	0.05	0.46
Cumin	2.1	0.47	0.101	0.12	0.21	0.25
Aniseed	2	0.30	0.036	0.09	0.12	0.30
B. pepper	2.1	0.07	0.118	0.05	1.68	0.77
Carraway	1.7	na	na	na	na	na
Chilli	1.8	0.31	0.261	0.04	0.84	0.13
Fenugreek	3.7	0.24	0.209	0.32	0.87	1.33

tsf= tea spoon ful. na= not available.

OCPs may find their way to human system through food and water. The organochlorine pesticide residues have also been detected in human diet (Kannan et al. 1992) , drinking water (Dikshith et al. 1990) and in herbal preparations (Srivastava et al 2000) . Pesticides are known to enter in plant products from contamination via spillage and volatalisation of residues from pesticide treated soils or storage. Though, the pesticides like HCH and DDT are well known toxic chemicals (WHO 1974, Bulger and Kupfer 1985, Hayes 1991), their residues were found at very low in all the samples of spices analysed. This level may even go much lower after frying and cooking of food. It is known that certain physical and chemical conditions like washing, heat treatment, steaming, treatment with supercritical carbon dioxide are known to reduce the level of pesticides (Stahl and Rau 1984; Nash 1984; Srivastava and Nath 1990).Even then, the spices should be monitored periodically as these products are exported in various countries.

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