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Monitoring of pesticide residues (DDT, HCH and ENDOSULPHAN) in cauliflower from West Bengal (INDIA)

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ABSTRACT

Residues of organochlorine pesticides (OCPs) were measured in cauliflower from West Bengal, India. The levels of OCPs were ranged between, 0.41 – 10.71 µg kg^{-1} (wet wt.), and the mean concentration of DDT, HCH and endosulphan was 3.31±0.52 µg kg^{-1} (wet wt), 2.63±0.61 µg kg^{-1} (wet wt), and 0.91±0.30 µg kg^{-1} (wet wt) respectively. The ratio of α-HCH to γ-HCH isomers (α/γ HCH ratio) ranged 0.09 to 3.37, which reflects the use of lindane as well as technical HCH. The ratio of p,p'-DDT/p,p'-DDE, p,p'-DDT/∑DDT and (DDE+DDD)/∑DDT, was 0.98, 0.27 and 0.66 respectively, indicates contamination with fresh input of aged mixture of DDTs. The cauliflowers from West Bengal had levels of OCPs much below than the MRLs, indicating minimal health risk to the consumers. However, it is recommended that regular intensive assessment for persistent organic pollutants to be conducted, due to human health concerns.

Keywords: DDT, HCH, endosulphan, Vegetable

INTRODUCTION

Indian agriculture sector is the backbone of the economy and constitutes 18% to the gross domestic production (GDP). Agriculture sector provides employment to 65% of Indian population. The total agriculture area is 123.22 million hectare, which accounts 43% of total geographical area of India. India rank second in wheat, rice, oilseeds and vegetable production in the world. India contributes about 17% of world vegetable production. Cauliflower (*Brassica oleracea botrytis*) is produced in many areas of India. During 2009-10, the total cultivation area of cauliflower was about 0.256 million hectares with annual production about 5.509 million tonnes [1].

Modern agriculture is dependent on high yielding varieties, which can only be grown under the influence of fertilizers and pesticides. Pesticides have been widely used in agriculture production in developed and developing countries. Among pesticides, organochlorine pesticides (OCPs) such as dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), and endosulphan are of much concern in the environment because of their prolonged persistence, long range transport nature, toxicity as well as tendency to accumulate in biota [2]. Organochlorine pesticide exposure has been associated with arthritis, cancer and diabetes [3-6]. The main non-occupational route of exposure to organochlorines is through dietary intake [7]. During 1970s and 1980s use of some OCPs has been banned or restricted in developed and developing countries. However, these are still in use in some developing countries including India, because of their low cost and versatility in industry, agricultural and public health.

India is the major pesticide producer in the world. The domestic production of pesticides is approximately 85 TMT (thousand metric tonnes), and about 50 TMT used annually where, 71% accounts for insecticides [8-10]. The consumption of pesticides in India is 0.5 kg/ha, comparatively low (only 3.75% of global consumption) against 12.0, 7.0, 6.6, and 3.0 $kg.ha^{-1}$ in Japan, USA, Korea and Germany, respectively [11]. In India, large quantities of organochlorine pesticides (OCPs), were produced and used in agricultural and public health. Indiscriminate use of pesticides leads to accumulation of pesticide residues in consumable vegetables. Contamination of vegetables with pesticide residues has been reported worldwide including India by several researchers [12-18]. Therefore, the occurrence of OCPs residues in Indian environment is widespread and has over the years sustained considerable research interest in environmental contamination status and human exposure in the country.

West Bengal, the eastern state of India with 51.23 lakh hectares of agricultural land, and produces 1.754 million tonnes of cauliflower annually on 57,000 hectares of land. Cauliflower is low in fat, high in dietary fibres; contain water, vitamin A, C, K and minerals, possessing a very high nutritional density. The cauliflower growers have been using the pesticides frequently to have the higher yield. During 2004-05, in West Bengal the technical grade pesticides of 4100 MT were used. Kolkata is the capital city of West Bengal where several studies have been conducted on organochlorine pesticides in different matrices including food commodities [19-23].

This paper deals with the study carried out on the residue levels of organochlorine pesticides (HCHs, DDTs, and endosulphan) in cauliflower from West Bengal, India. Further, we compare the observed concentrations of organochlorine pesticides in cauliflower with recommended maximum residual levels (EMRLs) proposed by government of India [24] and European commission [25].

MATERIALS AND METHODS

Sampling

Commercial samples of the cauliflower were collected from local vegetable markets of south 24, Paragnas district of West Bengal. Samples were collected in clean polyethylene bags, labelled and transported ice preserved to the laboratory. Samples were kept in refrigerator till further extraction. Only edible part was processed and analyzed for DDTs (o,*p'*-DDE, o,*p'*-DDD, *p,p'*-

DDD, *o,p'*-DDT and *p,p'*-DDT), HCHs (α-HCH, β-HCH, γ-HCH, and δ–HCH), and endosulphan (α- & β-) pesticides.

Chemicals and Solvents

Chemicals (sodium sulphate, silver nitrate, potassium hydroxide, activated charcoal and sulphuric acid) and solvents (acetone, methanol, dichloromethane, and hexane) were purchased from Merck India. Silica gel 60 (0.063 – 0.100 mm) was from Sigma-Aldrich. Prior to use, silica gel and anhydrous sodium sulphate was cleaned separately with methanol, dichloromethane and acetone in Soxhlet extractor for 8 h each, and stored air tight at 130^0 C. The preparation of acid silica, basic silica and silver nitrate impregnated silica gel were described elsewhere [26]. Pesticide standard solutions were obtained from Supelco (Sigma, USA).

Extraction of Samples

Samples were washed with deionised distilled water, dried on filter paper, cut into small pieces with the help of grater, and mixed thoroughly. Twenty grams of mixed sample was grinded with 10 -15g anhydrous sodium sulphate in warring blender. The grinded sample was extracted with 50 ml acetone on mechanical shaker for one hr. The acetone extract was filtered by employing vacuum suction and the process was repeated three times for complete extraction. The filtrate was concentrated to near 50 ml using Rotatory Vacuum evaporator (Buchi Germany) and subjected to liquid-liquid portioning with hexane in separatory funnel. Hexane layer with residues was collected passing through sodium sulphate. Aqueous phase was again subjected to hexane extraction (three times) for leftover residues. Pooled hexane fractions were concentrated to 10 ml.

Chromatography Column Clean-Up

Concentrated hexane extracts were passed through glass column containing activated charcoal and anhydrous sodium sulphate to clean the pigment contents. The multilayered silica gel column chromatography was performed for fractionation and to remove interfering sulphur, and other aliphatic compounds. Briefly multilayered silica gel column (300 mm x 30 mm) was packed from bottom up with 2.5 g silica gel, 4.0 g silver nitrate silica gel, 2.5 silica gel, 4.0 basic silica gel, 2.5 g silica gel, 12.0 g acid silica and 5.0 g anhydrous sodium sulphate. The column was pre-rinsed with 50 ml n-hexane before sample was loaded. The elution of analytes was subsequently carried out using 170 ml hexane and concentrated to 2.0 ml. The extract was transferred to sample vial and 2 µl was injected onto a gas chromatograph equipped with an electron capture detector (GC-ECD) for quantification.

Instrumental Analysis

Identification and quantification of pesticide compounds in extracted and cleaned samples were analyzed using gas chromatograph (Varian Star 3400cx, Australia) equipped with ^{63}Ni electron capture detector (ECD). Separation of OCP compounds was accomplished using a capillary column (RTX-5) with 0.25mm i.d. and 30 m and 0.5 µm of stationary phase (5% diphenyl-95% dimethyl polysiloxane). The column oven temperature program was as follows: The oven temperature was initially maintained at 170^0 C and programmed to increase at 7^0 C min^{-1} to 220^0 C and again ramped to 250^0 C at 5^0 C min^{-1} and held for 7.0 min. The injector and detector temperature were maintained at 250^0 C and 350^0 C respectively. A purified Nitrogen gas was used as carrier at the flow rate of 1.0 ml min^{-1}.

Analytical Quality Control

Certified reference standard solutions (Sigma,USA) were used for calibration of instrument. Resolved peaks were integrated using software. The concentrations of target compounds were determined by external standard method using the peak area of the samples and the five level calibration curves of the standards. The peak identification was conducted by the accurate retention time of each standard. Retention times and peak areas of the compounds were comparable with the relative standards. Appropriate quality assurance quality control (QA/QC) analysis was performed, including analysis of procedural blanks to check the cross contamination and interferences (analyte concentrations were <MDL 'method detection limit'), random duplicate samples (Standard deviation <5), five level calibration curves with the r^2 value of 0.999, calibration verification (standard deviation <±5), and matrix spiked. Sample was spiked with known working standard solutions of OCPs, then extracted and analyzed in the same way as the real samples. The percent recoveries were in range of 72-111 (±6-12) for studied pesticide compounds. The recoveries assumed to be satisfactory and the results were not corrected for the recovery. Each sample was analysed in duplicate and the average was used in calculations. The results of the analysis are reported in µg kg^{-1} wet -weight (wet wt.) basis. A reporting limit of > 0.01 µg kg^{-1} wet wt was taken for calculation. Levels below reporting limit or below MDL (<0.01 µg kg^{-1} wet wt) were taken as zero (0) in the calculations.

RESULTS AND DISCUSSION

Distribution of OCPs

The monitored OCPs are o,*p'*-DDE, o,*p'*-DDD, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT (DDTs), α-HCH, β-HCH, γ-HCH, and δ–HCH (HCHs), and endosulphan (α-& β-). The concentration of detected pesticide residues in cauliflower from West Bengal are presented in **Table 1**.

Table 1: Concentrations of organochlorine pesticides (µg kg^{-1} wet wt) in cauliflower from West Bengal, India (n=14)

Name of compound	Range		Mean	Median	SE*
	Min	Max			
α-HCH	<0.01	5.69	0.88	0.61	0.38
β-HCH	<0.01	0.20	0.08	0.08	<0.01
γ-HCH	<0.01	5.34	1.63	1.46	0.40
δ-HCH	<0.01	0.14	0.05	0.05	<0.01
∑HCH	**<0.01**	**7.97**	**2.63**	**2.51**	**0.61**
p,p'-DDE	0.11	6.29	1.93	1.34	0.54
o,p'-DDD	<0.01	1.46	0.36	0.20	0.11
p,p'-DDD	<0.01	0.16	0.09	0.10	<0.01
o,p'-DDT	<0.01	0.43	0.19	0.19	0.03
p,p'-DDT	<0.01	1.68	0.77	0.68	0.16
∑DDT	**0.25**	**6.52**	**3.31**	**3.37**	**0.52**
Endosulphan I	0.05	4.04	0.72	0.17	0.29
Endosulphan II	<0.01	1.60	0.19	0.08	0.11
∑Endosulphan	**<0.01**	**4.10**	**0.91**	**0.39**	**0.30**
∑OCPs	**0.41**	**10.71**	**6.87**	**7.49**	**1.46**

*Note: - * standard error= standard deviation /√n*

The ∑OCPs concentrations were ranged between 0.41 to 10.71 µg kg^{-1} (wet wt.) with the arithmetic mean of 6.87 µg kg^{-1} (wet wt.) and median 7.49 µg kg^{-1} (wet wt.). Among studied

OCPs, the DDT (3.37 µg kg^{-1} wet wt.) was the dominant contaminant followed by HCH (2.51 µg kg^{-1} wet wt.) and endosulphan (0.39 µg kg^{-1} wet wt.). DDTs alone accounts 48% of total OCP contamination followed by HCHs (39%) and endosulphans (13%) (**Figure 1**).

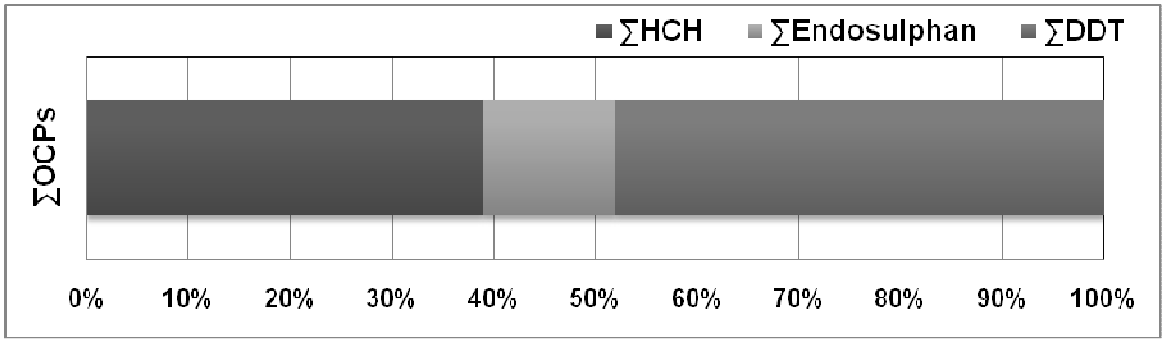

Figure 1: Percent distribution of OCPs (DDT, HCH and endosulphan) in cauliflowers from West Bengal (India)

The ∑DDT residue levels in cauliflower from West Bengal were in the range, 0.25 – 6.52 µg kg^{-1} (wet wt.), and the average concentration of DDT isomers were 1.34, 0.20, 0.10, 0.19 and 0.68 (µg kg^{-1} wet wt.) for o,*p'*-DDE, o,*p'*-DDD, *p,p'*-DDD, *o,p'*-DDT and *p,p'*-DDT, respectively. The DDT concentrations in cauliflower in this study were higher than from Agra, India, Deyang and Yanting, China, however lower than those from Haryana, India, Tianjin, China, Central Uttar Pradesh, India. The observed DDT concentrations in cauliflower from this study were far much lower than recommended maximum residual limits (MRLs) of DDT in cauliflower.

For HCH, the residue concentrations ranged from <0.01 to 7.97 µg kg^{-1} (wet wt.). The lindane (γ-HCH) compound is the highest in concentration (1.63 µg kg^{-1} wet wt) followed by α-HCH (0.88 µg kg^{-1} wet wt), β-HCH (0.08 µg kg^{-1} wet wt) and δ-HCH (0.05 µg kg^{-1} wet wt). The data of this study shows that ∑HCH levels in cauliflower from were comparable with the results from Meerut, Muzaffarnagar and Ghaziabad ad district of Uttar Pradesh, India, however lower than from Tianjin, China, Haryana, India and, cauliflower from cities of Central Uttar Pradesh, India but, higher than those from Deyang and Yanting, China, Agra, India (**Table 2**). This study indicates that residue levels of HCHs in cauliflower were far much below the MRLs set by European Commission and Indian government, indicating minimal risk to the consumers.

Table 2: Pesticide residues in cauliflower: comparison of this study with MRLs, regions and countries (µg kg^{-1})

Region, country	Name of organochlorine pesticides ∑HCH	∑DDT	∑Endosulphan	Reference
EC, MRLs	**50**	**50**	**50**	**[26]**
Indian, MRLs	**1000**	**3500**	**2000**	**[25]**
West Bengal, India	**2.63**	**3.31**	**0.91**	**Present study**
Deyang, China	0.17	0.39	-	[18]
Tianjin, China	38-65	30-65	-	[16]
Agra, India	2.49	2.33	-	
Haryana, India	34-520	18-25	29-60	[15]
Uttar Pradesh, India	2.51-8.50	-	-	[25]
Uttar Pradesh, India	9.80	35.50	4.05	[19]
Faisalabad, Pakistan	-	-	408	[17]

The observed concentration of endosulphan in cauliflower from West Bengal was 0.91 µg kg^{-1} wet wt (range, <0.01-4.10 µg kg^{-1} wet wt.) with α-endosulphan (0.72 µg kg^{-1} wet wt.) and β-endosulphan (0.19 µg kg^{-1} wet wt.). In the present study data shows that cauliflowers were less contaminated with Endosulphan when compared with vegetables from Faisalabad, Pakistan, Central Uttar Pradesh, India, and Haryana, India. This study shows that cauliflowers from West Bengal are safe for consumption when compared to MRLs (**Table 2**).

Compositional Analysis for Possible Sources of OCPs

It has been recognized that HCH is available in two formulations: technical HCH and lindane. Technical HCH contains isomers in the following percentage: α, 55-80%; β, 5-14%; γ, 8-15%; δ, 2-16%; ε, 3-5% [27], and Lindane contains >90% of γ-HCH. The ratio of α–HCH to γ–HCH (α/γ, ratio) has been used to identify the possible HCH source. The ratio of α-HCH to γ-HCH between 3 and 7 is indicative of fresh input of technical HCH [28]. However, a lindane source will show the reduced ratio close or <1. A higher ratio of α -HCH to γ- HCH than 7 can be explained by long-range transport or recycling of technical HCH, because α-HCH has longer atmospheric lifetime than γ-HCH by about 25% [29]. In this study, the overall average ratio of α-HCH to γ-HCH isomers (α/γ ratio) ranged 0.09 to 3.37 with a pooled mean of 0.89 which probably reflects the use of more lindane and, as well as less technical formulation of the HCH in the agriculture fields from where the cauliflowers have came to the market (**Table 3**).

Table 3: Isomer ratios of α/γ HCH, *p,p'*-DDT/*p,p'*-DDE, *p,p'*-DDT/∑DDT and DDE+DDD/∑DDT in cauliflower from West Bengal, India

Ratio	α/γ ratio (HCH)	*p,p'*-DDT/*p,p'*-DDE	*p,p'*-DDT/∑DDT	DDE+DDD/DDT
Range	0.09-3.37	<0.01-3.54	<0.01-0.57	0.28-1.00
Mean	0.89	0.98	0.27	0.66
Median	0.42	0.57	0.27	0.66

As per Stockholm Convention, the usage of DDT in agriculture has been banned but permitted to use (10,000 t/year) to combat vector borne diseases, until an alternative can be found [21]. Nearly 85% of the DDT produced in India is used for public health practices. During 2006-07, India used 6000 and 2560 MT of DDT for control of malaria and Kala Azar, respectively. DDT is known to biodegrade to DDE under aerobic and to DDD in anaerobic conditions. DDE and DDD changes in the ratio of DDE and DDD to DDTs has been regarded as an indication of either no or decreasing inputs to the environment. The vapour pressure of *o,p'*-DDT is 7.5 times greater than *p,p'*-DDT, and *p,p'*-DDT metabolize much faster in soils [30]. In the present study the amount of *p,p'*-DDT volatilized from the soil surface may be relatively small compared to *o,p'*-DDT. After the DDT applications were discontinued, much of the DDT may be converted to *p,p'*-DDE [31]. Higher concentration of *p'p*-DDE (1.93 µg kg^{-1} wet wt) has been interpreted as a result of DDT conversion to *p,p'*-DDE by UV radiation after prolong exposure in the environment [32]. The residence time of *p,p'*-DDT could be estimated using the ratio of *p,p'*-DDT to ∑DDTs. The *p,p'*-DDT/∑DDTs ratio for technical DDTs was reported to be 0.77 [33]. The ratio of *p,p'*-DDT/*p,p'*-DDE >0.5 may indicate recent input of DDT, and, in contrast, of <0.3 may imply past input DDT [34]. In this study the ratio of *p,p'*-DDT to ∑DDTs and .*p,p'*-DDT/*p,p'*-DDE was 0.27 and 0.98, respectively (**Table 3**). So, it is stipulated that the recent inputs of aged mixture of DDTs existed in the study area. In addition, a ratio of (DDE+DDD)/∑DDT >0.5 is indicative for a long-term biotransformation of DDT to DDD and DDE, while a ratio of less than 0.5 may be imply recent input [35]. The mean ratio of

(DDE+DDD)/∑DDT in the present study were 0.66, which indicates that these vegetables were probably contaminated with fresh input of aged mixture of DDTs.

Endosulphan is not considered as environmentally persistent compound [36]. However, it is toxic to aquatic organisms [37] and classified as a class II component (moderately hazardous) by the World Health Organization. India is the major producer of endosulphan and annual consumption was 3600t [23]. Endosulphan alone accounts for over 10% of the total insecticide consumption in India. Endosulphan consists in two isomers, α and β, in the ratio of 7:3. In West Bengal, technical endosulphan had been used for a longer period for pulse crop, Bengal gram [20]. Earlier, elevated concentrations of endosulphan have been reported in ambient air, coastal sediment and fishes from West Bengal.

CONCLUSION

The analysis of cauliflower from West Bengal, India has demonstrated a quite low level of contamination by organochlorine pesticides, which generally never exceeded the residue levels of OCPs set by European Commission and Indian government indicating minimal risk to the consumers. However, a frequency of presence of the OCPs in vegetable was observed and is a matter of concern since organochlorine pesticides are known to accumulate in biota. Vegetables are important components of Indian diet, and even low levels of pesticides in vegetables may have adverse effects in the consumers. The study indicates the use of lindane as well as technical formulation of the HCH in the study area and, contamination of these vegetables with aged mixture of DDTs more recently. This may be happens by transportation of pollutants from nearby human settlement areas, where pesticides used for public health aspects. Therefore, identification and elimination of contamination sources of OCPs in vegetables is recommended for the protection of human health.

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