

ASSESSMENT OF ORGANOCHLORINE PESTICIDE RESIDUES IN NORTHERN LIGHT SOILS OF FCV TOBACCO IN ANDHRA PRADESH

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The study was conducted to assess the organochlorine pesticides in FCV tobacco growing Northern Light Soil (NLS) area of Andhra Pradesh. The gas chromatography-mass spectrometry (GC-MS) for detection and quantification of eleven organo-chlorine pesticide residues (α -HCH, β -HCH, γ -HCH, δ -HCH, chlorpyrifos, endrin, α -endosulfan, β -endosulfan, endosulphate, 2,4-DDT, and 4,4-DDT) in soil samples. The concentration of α -HCH varied from 0.001 to 0.014 $\mu\text{g/g}$ (Mean value: 0.003 $\mu\text{g/g}$). While the β -HCH and γ -HCH are in the range of 0.003 to 0.025 $\mu\text{g/g}$ and 0.001 to 0.018 $\mu\text{g/g}$, respectively. The mean value of total BHC (α -HCH, β -HCH, γ -HCH) was 0.0162 $\mu\text{g/g}$. The mean value of Chlorpyrifos concentration was 0.03 $\mu\text{g/g}$, while the mean Endrin concentration was 0.008 $\mu\text{g/g}$. The Endosulfate content ranged from 0.004 to 0.075 $\mu\text{g/g}$ with a mean value of 0.032 $\mu\text{g/g}$. Total organochlorine pesticide residues in northern light soils varied from 0.036 (*Sangayagudem*) $\mu\text{g/g}$ to 0.449 $\mu\text{g/g}$ (*Dhrabhagudem*) with a mean value of 0.126 $\mu\text{g/g}$. The pesticide residue concentrations found in the studied FCV tobacco grown soils were below the Maximum Residue Limits (MRL) varying from 0.1 to 8.0 ig/kg set by Food and Agriculture Organization of the United Nations (FAO). The detected pesticide residues reflected the type of pesticides that may have been used in the past in the study areas. Hence, it is concluded from the study that the FCV tobacco grown under NLS area is free from Organochlorine Pesticide residues.

Keywords: Pesticides, FCV Tobacco, Soil, Residues, GC-MS

INTRODUCTION

Persistent Organic Pollutants (POPs) are those compounds which persist long time and mobile in the environment and become bio toxic in food chains. Due to the global concern, organochlorine pesticides (OCPs) will have

concentration, as OCPs had been widely applied in agricultural fields around the world for decades until they were banned in 2010 (Yu Liu et al., 2014). Despite the banning of most of these chemicals, these OCPs often detected in various environments and in many places due to their high persistence. As a consequence, any pesticide that is present in soil can potentially be incorporated into growing crops. Contaminated soil also represents a serious environmental problem as the pesticides are movable to other environmental systems such as ground water and air. Soil is a complex matrix which consists of organic and inorganic material. Soil matrix is more difficult to extract and require longer extraction times due to the stronger interactions that may occur between the soil and the pesticides (Pszczolińska et al., 2017). It possesses many active ingredients (polar, non polar and ionic) that are capable of retaining pesticides and other residues. Pesticide leaching or drainage from cultivated land into the surface waters and underlying ground water are a source of pollution because of their environmental mobility and persistence (Abong'O Deborah Atieno et al., 2015). The aim of this study was to assess the organochlorine pesticide content in FCV tobacco growing northern light soils (NLS) of Andhra Pradesh. Eleven organochlorine pesticides, comprising various chemical properties, were used for the study.

MATERIALS AND METHODS

Collection of soil samples

The soil samples were collected from 25 different villages representing each sample a village from NLS area. viz., *Yarnagudem*, *Ramannapalem*, *Sangayagudem*, *Bandapuram*, *Kothagudem*, *Buttaigudem*, *Ramanujapuram*, *Nagulagudem*,

Antharvedigudem, Doramamidi, Bandivarigudem, Vegavaram, Gangineedupalem, Darbagudem, Ootasamudram, Pothavaram, Dippakayalapadu, Kandrikagudem, Koyyalagudem, Bayyanagudem, Gopalapuram, Dondapudi, Vedullakunta, Peddapuram and Yadavolu. The samples were air dried, processed and analyzed.

Sample extraction

5 g of soil was taken in a 150-ml Erlenmeyer conical flask, and 25 ml of acetonitrile and water (2:1) mixture and 50 ml of 5% sodium chloride mixture was added to the flask. The samples were kept overnight and filtered with 'Whatman No.1' filter paper. The filtrate was partitioned with 40 mL of hexane, and the hexane fraction was collected for clean-up. A column was prepared by preparing a column bed which was made of 2 g florisil (60/100 mesh) sandwiched between two layers of anhydrous sodium sulphate. Before clean-up, the column was eluted with pure hexane. The hexane fraction was collected from the column and evaporated to dryness under reduced pressure.

Preparation of standard solutions

The stock solutions of the selected pesticide standards were prepared by 10 mg of each pesticide dissolving in 10 ml acetone. A working standard mixture of $1 \text{ } \mu\text{g ml}^{-1}$ was prepared and calibration standards (0.0078, 0.0156, 0.0312, 0.0625, 0.125 and $0.25 \text{ } \mu\text{g ml}^{-1}$) were prepared by serial dilution with acetone.

Estimation of pesticide residues

The extracted fraction from soil was estimated using single quadrupole GC-MS-QP-2010 Plus (Shimadzu Corporation, Japan) and the GC system (GC 2010 Plus) equipped with ZB-5 capillary column and autosampler. One μl of the sample was injected to GC-MS and the identification of each residue and quantification was done with the help of selective ion monitoring (SIM) in electron impact (EI) method.

RESULTS AND DISCUSSION

Soil samples were collected from 25 different villages representing each sample a village from

four different regions of Northern soil area of FCV tobacco were covered for the study. The samples were analysed for eleven organochlorine pesticide viz., α -HCH, β -HCH, δ -HCH, γ -HCH chlorpyrifos, endrin, α -endosulfan, β -endosulfan and endosulfan sulphate, 2,4-DDT, 4,4-DDT residues by GC-MS.

All the eleven pesticides were identified in the soil samples analysed (Fig.1). Most of these organochlorine pesticides are banned and are not recommended for in the cultivation of tobacco in India (Rakesh Kumar Ghosh *et al.*, 2014). The concentration of α -HCH varied from 0.001 to 0.014 $\mu\text{g/g}$ (Mean: 0.003 $\mu\text{g/g}$). While the β -HCH (Mean: 0.010 $\mu\text{g/g}$) and δ -HCH (Mean: 0.004 $\mu\text{g/g}$) are in the range of 0.003 to 0.025 $\mu\text{g/g}$ and 0.001 to 0.018 $\mu\text{g/g}$, respectively. The mean value of total BHC (α -HCH, β -HCH, δ -HCH) was 0.0162 $\mu\text{g/g}$. The highest total BHC concentration of 0.054 $\mu\text{g/g}$ was observed in the soil sample from *Gangineedupalem* village. The α -HCH varied from 0.001 to 0.012 $\mu\text{g/g}$ (0.002 $\mu\text{g/g}$).

Chlorpyrifos concentration was 0.014 to 0.058 $\mu\text{g/g}$ with a mean value of 0.03 $\mu\text{g/g}$. The highest chlorpyrifos residue value was observed in the sample from village *Dhrabagudem* (0.058 $\mu\text{g/g}$). Endrin concentration ranged between 0.001 to 0.032 $\mu\text{g/g}$ with a mean value of 0.008 $\mu\text{g/g}$ (Tab.1). Endosulfon-I varied from 0.003 to 0.053 $\mu\text{g/g}$. Mean value was 0.018 $\mu\text{g/g}$. The Endosulfon-II ranged between 0.001 to 0.034 $\mu\text{g/g}$ (Mean: 0.004 $\mu\text{g/g}$). Endosulfate content in soil sample ranged from 0.004 to 0.075 $\mu\text{g/g}$ with a mean value of 0.032 $\mu\text{g/g}$ for NLS. Similarly, Abong'O Deborah Atieno *et al.*, 2015, found endosulfan sulfate which

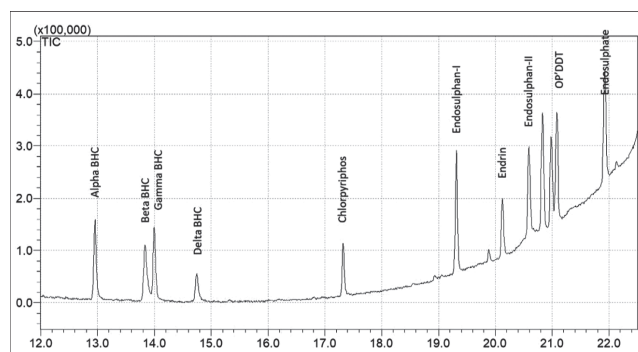


Fig.1: Total Ion Chromatogram (TIC) of the pesticides identified in the soil samples.

Table 1: Status of pesticide residues in FCV tobacco growing soils of NLS area in Andhra Pradesh.

S. No.	Village	α -HCH	β -HCH	δ -HCH	γ -HCH	Chlorpyrifos	Endrin	Endo sulphan-1	Endo sulphan-II	Endo sulphate	OP DDT	PP DDT	OPC
1	Yarnagudem	0.001	0.006	0.001	BDL	0.018	0.00	0.003	0.001	0.004	BDL	BDL	0.038
2	Ramannapalem	0.001	0.005	0.001	0.002	0.020	0.003	0.005	BDL	0.008	BDL	BDL	0.048
3	Sangayagudem	BDL	0.004	BDL	BDL	0.018	0.001	0.010	BDL	0.006	BDL	BDL	0.045
4	Bandapuram	BDL	0.003	BDL	BDL	0.014	BDL	0.003	BDL	0.009	0.001	BDL	0.036
5	Kothagudem	0.003	0.009	BDL	BDL	0.023	0.019	0.009	BDL	0.011	BDL	BDL	0.079
6	Buttaigudem	0.001	0.009	0.002	BDL	0.031	0.007	0.024	BDL	0.044	BDL	BDL	0.122
7	Ramanuja Puram	0.002	0.011	0.002	BDL	0.028	0.013	0.006	0.001	0.045	BDL	BDL	0.111
8	Nagulagudem	0.001	0.006	0.001	BDL	0.030	0.003	0.016	0.003	0.030	0.001	BDL	0.093
9	Antharvedigudem	0.001	0.008	0.002	BDL	0.038	0.009	0.018	BDL	0.026	0.001	BDL	0.106
10	Doramamidi	0.004	0.009	0.005	0.001	0.035	0.005	0.022	0.005	0.034	0.017	0.016	0.153
11	Bandivarigudem	0.002	0.010	0.003	BDL	0.041	0.011	0.011	0.003	0.026	BDL	BDL	0.11
12	Vegavaram	0.001	0.008	0.001	BDL	0.026	0.003	0.009	0.002	0.019	BDL	BDL	0.072
13	Gangineedupalem	0.014	0.022	0.018	0.010	0.025	0.019	0.038	0.022	0.046	0.037	0.031	0.282
14	Darbagudem	0.005	0.011	0.012	0.005	0.058	0.032	0.033	0.034	0.075	0.098	0.086	0.449
15	Oootasamudram	0.001	0.008	0.002	BDL	0.030	0.005	0.023	0.001	0.041	0.002	BDL	0.115

BDL: Below Detectable Limit

OP1: Ortho para PPI; Para para

Continued...

Table 1: Status of pesticide residues in tobacco growing soils of NLS area in Andhra Pradesh.

S.No	Village	α -BHC	β -BHC	δ -BHC	γ -BHC	Chlorpyrifos	Endrin	Endo sulpham-I	Endo sulpham-II	Endo sulphate	OP ⁱ DDT	PF DDT	Total OPC
		(μ /g)											
16	Pothavaram	0.001	0.007	0.001	BDL	0.021	0.002	0.013	BDL	0.022	0.001	BDL	0.071
17	Dippakayalpadu	0.008	0.013	0.006	0.006	0.028	0.002	0.021	0.005	0.041	0.005	0.004	0.139
18	Kandrikagudem	0.002	0.009	0.002	BDL	0.028	0.006	0.053	BDL	0.027	0.001	BDL	0.131
19	Koyyalagudem	0.002	0.025	0.002	0.012	0.034	0.007	0.019	0.009	0.035	0.017	0.018	0.18
20	Bayyanagudem	0.007	0.013	0.012	0.005	0.026	0.006	0.021	0.009	0.032	0.009	0.010	0.15
21	Gopalapuram	0.004	0.008	0.004	0.001	0.024	0.001	0.015	0.001	0.020	0.002	0.002	0.082
22	Dondapudi	0.003	0.011	0.004	0.002	0.037	0.014	0.021	0.001	0.032	0.002	0.003	0.13
23	Vedullakunta	0.001	0.007	0.002	BDL	0.029	0.002	0.011	BDL	0.014	BDL	BDL	0.07
24	Peddapuram	0.002	0.008	0.003	BDL	0.033	0.006	0.032	0.001	0.090	0.016	0.003	0.195
25	Yadavolu	0.003	0.010	0.004	0.001	0.042	0.018	0.012	BDL	0.062	0.001	0.001	0.155
	Mean	0.003	0.010	0.004	0.002	0.030	0.008	0.018	0.004	0.032	0.009	0.008	0.126
MRL for soils (FAO, 2000)		0.2	0.1	-	-	-	0.2	-	-	-	-	8.0	
GRL for leaf Tobacco		Total BHC: ($\alpha + \beta + \delta$) = 0.07		0.50	0.50	0.50	0.05	Total Endosulphan = 1.00		Total DDT=0.20			
		ND: Non-Detectable		OP ⁱ : Ortho para PP ⁱ : Para para		GRL: Guidance Residue Level.							

BDL: Below Detectable Limit OPⁱ: Ortho para PPⁱ: Para para
 ND: Non-Detectable OPⁱ: Ortho para PPⁱ: Para para GRL: Guidance Residue Level.

is a degradation product of Endosulfan was also detected in the soils of Kenya.

The total Endosulphan concentration and total DDT contents were highest in *Dhrabhagudem* village (0.142 µg/g and 0.184 µg/g, respectively). OP DDT varied from 0.001 µg/g to 0.098 µg/g (Mean value: 0.009 µg/g). PP DDT content ranged between 0.001 to 0.086 µg/g (Mean value: 0.008 µg/g). Total organochlorine pesticide residues in northern light soils varied from 0.036 µg/g (*Sangayagudem*) to 0.449 µg/g (*Dhrabhagudem*). The mean value of total Organochlorine Pesticide residue of NLS area was 0.126 µg/g. The list of villages collected samples and pesticide concentrations (ug/g) are presented (Table 1).

The pesticide residue concentrations found in the studied FCV tobacco grown soils were below MRL varying from 0.1 to 8.0 ig/g set by Food and Agriculture Organization of the United Nations (FAO) and are also within the Guidance Residue Level limits (GRL) specified for FCV tobacco. Routine monitoring of pesticide residues is necessary for the prevention, control and reduction of environmental pollution, leading to minimize health risks according to OCP residue studies conducted in soils of Togo by Lankondjoa Kolani *et al.*, 2017. The assessment study and results obtained on eleven chlorinated pesticide residues (α-HCH, β-HCH, γ-HCH (lindane), δ-HCH, chlorpyrifos, 2,4-DDT, 4,4-DDT, endrin, α-endosulfan, β-endosulfan and endosulfan sulphate) in soils of FCV tobacco concluded that the levels of organochlorine pesticide residues in tobacco growing soils of NLS area in Andhra Pradesh are very low and negligible, the levels were below the MRL prescribed by FAO, (2000) for soils and are also within the Guidance Residue Level limits (GRL) specified for FCV tobacco. Since the residue levels in FCV tobacco soils under the study area are negligible, the scope of accumulation of organochlorine pesticides in the tobacco crop is minimal. Hence, it is concluded from the study that the FCV tobacco grown under NLS area is free from Organochlorine Pesticide residues.

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