

# Organochlorinated Pesticides Concentration Levels in Green Coffee Bean from Oromia, Ethiopia

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**Abstract:** Ethiopia is a country whose half of GDP lies on agricultural products. It is the birthplace of coffee Arabica. The use of pesticide is increasing worldwide, and particularly among rural populations of the developing world whose economy relies mostly in agriculture. Thus, contamination of the environment with pesticides and the pesticides entry into the food chain is unavoidable especially in developing countries. A study was conducted to investigate Organochlorinated pesticides residue levels in coffee beans commodities from Oromia region, Ethiopia. HRGC/HRMS was used for the determination of 23 organochlorine pesticides compounds in all samples. The extraction and clean up were done based on QuEChERS methods with slightly modification.  $\Sigma$ HCH,  $\Sigma$ Aldrin, heptachlor, Endrin,  $\Sigma$ Chlordane and Mirex were not detected in all of green coffee beans. Gamma-HCH, heptachlor, trans-chlordane, o,p'-DD, p,p'-DDE, o,p'-DDD, p,p'-DDD, o,p'-DDT and p,p'-DDT were detected at BQL. DDT and their metabolites were detected in most of coffee samples ranged 0.062ng/g to 51.7ng/g. Para, para'-DDT isomer was the dominant contaminant in green coffee beans. Our finding results obtained in this study provide vital information for the control and address further significance of researches on Organochlorinated pesticides in Ethiopia.

**Keywords:** Coffee; OCPs; Concentration and Ethiopia.

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## 1. INTRODUCTION

The use of pesticides to control pests and disease is important for the production of sufficient quantities in order to keep public health and maintain food security for dramatically increasing population like Ethiopia. However, the use of these agents sometimes leaves residues in/on plant parts used as human food or animal feed commodities. These residues may enter the human food chain either directly through the consumption of treated foods and from the environment. For the protection of human health and the environment, pesticide residues are routinely monitored in food, water, soil, and tissue samples. Developed countries have been set acceptable residue limits for various foods and environmental samples that play vital role for import and export on food products.

Population growth, land degradation and post-harvest loss are challenges to overcome food insecurity and sustainable food production in Ethiopia. Thus, Ethiopian government and nongovernmental organizations have working together to overcome prevailing challenges. The average losses of crops due to pests were estimated to reach between 30 to 40 % annually. As result, pesticides were promoted to protect and increase agricultural production so far. The most commonly used pesticides in Ethiopia are organophosphates, carbamates and to some extent organochlorides [1].

Although chemical pesticides use in Ethiopia was historically low, recent developments in increased food production and expansion in floriculture industry have resulted in higher consumption of chemical pesticides. Pesticide use in Ethiopian State farms is estimated at 7.76kg/hector/year, and less than 0.1kg/hector/year in smallholder farms (estimated 95 % of farm in Ethiopia). Only cotton on commercial farms uses 90% of imported insecticides. Government extension services promote packages of chemical inputs to improve the productivity of smallholder agriculture and achieve food security [2].

Ethiopian government signed STOCHOLM CONVENTION on 17 May, 2002 and got ratification, acceptance and approval on 09 June 2003. Since then all of 12 dirty persistent organic pollutants chemicals were banned. However, DDT is still on using for controlling of malaria diseases. According to Ethiopian government national implementation plan for the Stockholm Convention report in 2006, no reliable data or record of past imports and use of Annex A POPs (aldrin, chlordane, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), lindane, mirex, polychlorinated biphenyls, etc) exists in the country and it is difficult, therefore, to determine the extent of their use in the past. Ethiopia has not produced or exported Annex A POPs pesticides to date. However, they have been imported and used in the country in the past as evidenced by a significant amount of such pesticides found as stockpiles and wastes (obsolete pesticides) in some parts of Ethiopia during the inventory phase of the national implementation plan (NIP) preparation [3].

In the fact that problems of pesticides use in Ethiopia are miss-application of pesticides by farmers (over use, under use, miss-use and miss-handling), inappropriate providing of pesticides from inside and outside (export and distribution) in the country, lack of strong sustainable monitoring and evaluation of pesticides throughout the country, lack of trained man power and capitals to do continuous assessment and to manage properly on the use and effects of pesticides. Tadesse Amare and Asferachew Abate reported that considering the absence of effective controlling mechanisms in pesticides imports and their increased and inappropriate use in Ethiopia, an assessment of the impact on human health and ecosystem is warranted [4].

This may pollute the environment and affect the public health. In other side, it also affects export capacity of agricultural products to other country because of the requirement maximum residues limits in food products in once country's standard. Unfortunately, Ethiopian coffee imported to Japan had  $\gamma$ -HCH 0.002ppm (53 times), DDT 0.01ppm (2 times), Chlordane 0.01ppm (5 times), Heptachlor 0.01ppm (16 times) residue contaminations problem in 2008 (Table 1). Japan import about 25% of Ethiopian coffee, but since 2007/2008 going to prohibit import of Ethiopian coffee because high amount of pesticide residues levels was obtained in coffee and coffee's bag [5]. This may affect the economy of the producer (Ethiopia). Ethiopian government reacted and working on the issue in order to solve that problem, though the source of contaminations was unclear yet.

Ethiopia is a country whose half of GDP is lie on agricultural products. According to GDP-composition by sector-agriculture (%) 2012 country ranks, Ethiopia ranked 8<sup>th</sup> from the world with the value of 49.30 [6]. The agricultural sector employs 85% of the population and contributes about 80 % of the country's exports. Coffee is one the most export products and providing high capital income for Ethiopian's. Ethiopia, the birthplace of coffee Arabica and arguably the world's oldest coffee exporter, was the world's fifth largest coffee producer and eighth largest coffee exporter in 2007. It brings valuable foreign currency to a government that is revenue poor and coffee has been referred to as Ethiopia's "Black Gold". Still, nearly all coffee bean production is done by hand. Smallholders represent 95% of total production in a low-input, low-output system, making Ethiopian coffee production naturally 'organic', while state-owned and private-investor plantations account for 4.4% and 0.6%, respectively [7].

Management practices and intensities mostly depend on farmers' individual preferences and are rarely coordinated. The use of manure, fertilizers or pesticides is not common. Post-harvest processing comprises different steps and procedures. Coffee quality is the result of various factors, like the natural environment ('terroir'), the varieties used, management and cultivation practices, harvesting, post-harvest treatments, processing. The Ethiopian grading and classification system reflects these countless different combinations of the factors. Some of these factors, especially the cultivation and processing, can be influenced through training and capacity building. However, due to the inhomogeneous production and supply systems, low quality awareness and information at producer level, as well as due to the lack of processing infrastructure and skills, quality varies to a large extent [8]. Therefore, the main objective of the study was to identify and quantify pesticides concentration levels in green coffee beans.

## 2. MATERIALS AND METHODS

### 2.1. Description of the study area and sample collection:

Ethiopia is located on Horn of Africa at 9<sup>o</sup>08'42.00"N, 40<sup>o</sup>29'22.82"E, and 4736ft. Oromia is one of among nine regions in Ethiopia and found at 7<sup>o</sup>32'45.74"N, 40<sup>o</sup>38'04.87"E and elevation 5264. Eleven (11) green coffee beans samples were randomly collected from local market from Addis Ababa (2 samples), Nemet (5 samples), and Jimma (4 samples) cities. Each samples were packed in to polyethylene bag and stored in cooler box in Ethiopia prior brought to Japan during May - June, 2011 and stored in a refrigerator (-20 °C) till analysis as illustrated from the following Figure 1.

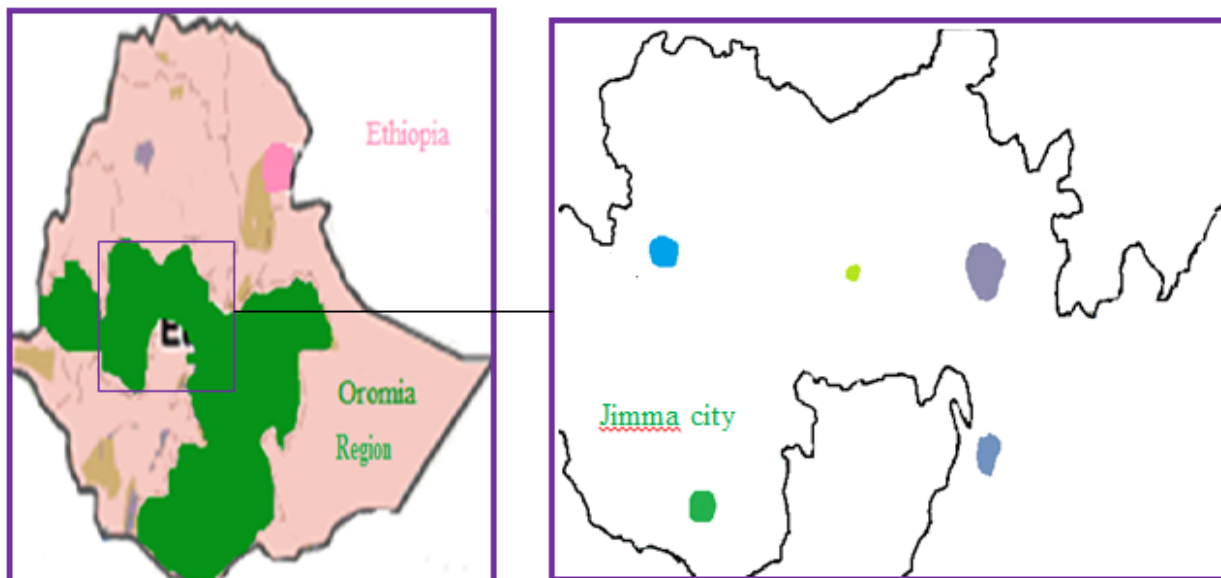


Figure 1: Map of Sampling Sites, Oromia Region, Ethiopia

## 2.2. Chemicals and Apparatus:

$^{13}\text{C}$ -POPs solution and  $^{13}\text{C}$ -Mono-Deca PCBs EC-4/89-A (Clean-up spike), were obtained from Cambridge Isotope Laboratories, Inc. MA, USA (Refer appendix). Acetonitrile, hexane, acetone, toluene, sodium chloride (NaCl),  $\text{Na}_2\text{SO}_4$  were obtained from Wako Pure Chemical Industries, Ltd, Japan. Magnesium Sulfate anhydrous ( $\text{MgSO}_4$ -anhydrous), disodium hydrogen citrate, trisodium citrate dehydrate, chloroform, and silica were obtained from Kanto Chemical C. Inc., Japan. Discovery DSC-18 1gram and ENVI-Carb 120/400, and PSA (Primary secondary amine) bonded silica were obtained from supelco, Bellefonte, PA, USA.

## 2.3. Methodologies:

### 2.3.1. Sample Extraction, Purification and Clean Up for Green Coffee Beans

Each sample were homogenized by sample homogenizer prior to analysis and stored at  $-20^\circ\text{C}$  in a refrigerator until analysis. Extraction was carried out mainly by following QuEChERS methods [9] with some modification. 5 grams were measured in to a 50ml centrifuge tube. 1000pg of each  $^{13}\text{C}$ - POPs labeled standards as clean up spike, acetonitrile 20 ml and hexane washed water 15ml were added and shaken by hand for 3 minutes. Buffer solution disodium hydrogen citrate 0.5 g, trisodium citrate dihydrate 1g, Sodium chloride 1g and anhydrous magnesium sulfate 4g were added and shaken for 3 minutes by hand. The mixture was gone to centrifuge separation at 3500 rpm for five minutes. The upper solution (acetonitrile) was taken and dried with anhydrous sodium sulphate. Again acetonitrile 20ml was added to solid residue and shaken for three minutes and repeated centrifuge separation. Extrude acetonitrile solution was concentrated to 1-3ml by rotary evaporator and passed to 10ml test tube, and further filled with acetonitrile.

Two ml aliquot extract solution was cleaned up with DSC-18 of 1 gram column by preconditioned and co-eluted with acetonitrile 10ml each. The elute solution was concentrated by rotary evaporator and changed to hexane solvent. Followed, ENV Carb 500mg and Primary Secondary Amine (PSA) 500mg were used for clean up after preconditioned and co-eluted each with 15 % acetone/hexane 10ml and 20ml respectively. It was collected then evaporated and concentrated under a gentle stream of nitrogen gas to  $50\mu\text{l}$ . 500pg of  $^{13}\text{C}$ -labeled total PCBs was spiked to the extract solution and further concentrated to  $50\mu\text{l}$  under a gentle stream of nitrogen gas.

### 2.3.2. HRGC/HRMS Conditions for Organochlorine Pesticides Residue Analysis

Identification and Determination were carried out by High Resolution Gas Chromatograph and High Resolution Mass Spectrometer (HRGC/HRMS). Conditions of HRGC/HRMS were shown in Table 1.

**Table 1: HRGC/HRMS Conditions during OCPs Analysis.**

HRGC	Gas chromatograph	Hewlett Packard Agilent 6890 series
	Column	HT8-PCB(60m Length, 0.25mm I.D., 0.25um film thickness, SGE)
	Inlet injector temperature	220°C
	Oven temperature	120°C(1min) - 20°C/min → 180°C- 2 °C/min→ 210°C -5°C /min → 310(5min)
	Injection mode	Split less
	Carrier gas	Helium,
	Column flow rate	1.5ml/min
	Injection volume	2µL
HRMS	High resolution mass spectrometer:	JEOL M-station 800D
	Detector temperature	280 °C
	Ionization mode	Electron Ionization, EI <sup>+</sup>
	Ionization current	500 µA
	Ion source temperature	280 °C
	Acceleration voltage	10kV
	Selected Ion monitoring	SIM
	Resolution	10,000

OCPs were analyzed by HRGC/HRMS using grouping point method based on retention time of each target compound. Table 2 shown retention time, accurate mass (m/z) value of each target compound, and as well as grouping point of OCPs by HRGC/HRMS analysis. Monitor ions 1 and 2 were used for calculation of each OCP in the samples by SIM chromatogram average of those two ions. Finally, data procurement was controlled by JEOL Diok program.

**Table 2: The retention time, m/z value of each target compound, and grouping point of HRGC/HRMS Analysis**

POPs Isomers	Group	Retention Time( min)	m/z	
			1	2
α-HCH	1	12.928	216.915	218.912
HCB	1	13.270	246.844	248.841
γ-HCH (Lindane)	1	14.798	216.915	218.912
β-HCH	1	15.087	216.915	218.916
δ -HCH	1	16.820	216.915	218.916
Heptachlor	1	17.525	271.810	273.807
Aldrin	1	19.938	264.854	262.857
Oxychlordan	2	22.078	388.805	388.802
Cis-Heptachlor Epoxide	2	22.421	352.844	354.841
Trans-Heptachlor epoxide	2	22.709	352.844	354.841
o,p'-DDE	3	23.957	315.938	317.935
Trans- Chordane	3	24.142	372.826	374.823
Trans-Nonachlor	3	24.400	406.787	408.784
Cis-Chlordane	3	24.731	372.826	374.823
p,p'-DDE	4	25.851	246.997	315.938
Dieldrin	4	26.076	264.854	262.857
o,p'-DDD	4	26.575	235.008	273.005
Endrin	4	27.470	264.854	262.857
o,p'-DDT	4	27.986	235.008	273.005
Cis-Nonachlor	4	28.125	262.857	264.854
p,p'-DDT	4	28.737	235.008	273.005
p,p'-DDT	4	30.130	235.008	273.005
Mirex	5	33.261	271.810	273.807
<sup>13</sup> C-α-HCH	1	12.911	222.935	224.932
<sup>13</sup> C-HCB	1	13.262	252.864	254.861
<sup>13</sup> C-γ-HCH (Lindane)	1	14.783	222.935	224.932
<sup>13</sup> C-β-HCH	1	15.071	222.935	224.932
<sup>13</sup> C-2CB(PCB #15)	1	15.071	234.041	236.038
<sup>13</sup> C- δ -HCH	1	16.800	222.935	224.932
<sup>13</sup> C-Heptachlor	1	17.501	276.827	278.824
<sup>13</sup> C-Aldrin	2	19.905	271.878	269.881

POPs Isomers	Group	Retention Time( min)	m/z	
			1	2
<sup>13</sup> C-Oxychlordane	2	22.052	396.839	398.836
<sup>13</sup> C-Cis-Heptachlor Epoxide	2	22.395	362.878	364.875
<sup>13</sup> C- <i>o,p'</i> -DDE	3	23.939	327.978	327.978
<sup>13</sup> C- <i>Trans</i> -Chordane	3	24.118	382.860	384.857
<sup>13</sup> C- <i>Trans</i> -Nonachlor	3	24.377	416.821	418.818
<sup>13</sup> C- <i>p,p'</i> -DDE	4	25.834	327.978	327.978
<sup>13</sup> C-Dieldrin	4	26.048	271.878	269.881
<sup>13</sup> C- <i>o,p'</i> -DDD	4	26.557	247.048	249.045
<sup>13</sup> C-Endrin	4	27.446	271.878	269.881
<sup>13</sup> C- <i>o,p'</i> -DDT	4	27.968	247.048	249.045
<sup>13</sup> C- <i>Cis</i> -Nonachlor	4	28.104	267.883	269.881
<sup>13</sup> C- <i>p,p'</i> -DDT	4	28.720	247.048	249.045
<sup>13</sup> C- <i>p,p'</i> -DDT	4	30.113	247.048	249.045
<sup>13</sup> C-Mirex	5	33.243	276.827	278.824

### 2.3.3. Determination of Method Validity:

#### Blank Sample Analysis:

A procedural blank sample was analyzed as same as methodologies for target matrix analysis to evaluate entrance and contamination. The recovery ratio of blank samples analyzed to assure and control the quality of the measured data for OCPs in green coffee beans samples range from 58 % to 100 % as shown in Table 4. The blank values are almost zero; therefore, there were no any contaminations in above two blank sample analysis.

#### Calibration Curve for the Determination of the Analyses:

The standard curve was obtained by using 0.5, 2, 10, 50, and 100ppb concentrations of OCPs standards. These five standard solutions were injected three times into a HRGC-HRMS for the calibration curve.

#### Detection and Quantification Limit:

For confirmation of minimum limit of detection (LOD<sup>m</sup>) and minimum limit of quantification (LOQ<sup>m</sup>) for method; only standard solution was used instead of the samples and all treatments has been done as same as for the sample according to the above procedure. Finally, 2µl of the extract solution was injected into HRGC/HRMS. It was done five times and the average and standard deviation were calculated. The LOD<sup>m</sup> and LOQ<sup>m</sup> for method were taken as three fold of standard deviation and tenfold of standard deviation respectively. For confirmation minimum limit of detection (LOD) and minimum limit of quantification (LOQ) for sample; LOD<sup>m</sup> and LOQ<sup>m</sup> of native standard isomers were taken from value of method and calculated according to the following formula. The result of LOD and LOQ for samples for OCPs was shown in table 3.

$$LOD = LOD^m \times (v/v_i) \times (V_E/V'_E) \times (1/V)$$

$$LOQ = LOQ^m \times (v/v_i) \times (V_E/V'_E) \times (1/V)$$

Where, LOD = Minimum limit of detection for the sample (pg/L)

LOQ = Minimum limit of quantification for the sample (pg/L)

LOD<sup>m</sup> = Minimum limit of detection for the methods (pg)

LOQ<sup>m</sup> = Minimum limit of quantification for the methods (pg)

v = Volume of the sample solution (µl)

V = Sampling volume of the sample (g)

v<sub>i</sub> = Injecting volume into GC/MS (µl)

V<sub>E</sub> = Volume of extracted solution (ml)

V'<sub>E</sub> = Aliquot volume of extracted solution (ml)

(Source: JIS K 0311, 2005)[10]

**Table 3: LOD and LOQ for each OCPs Analysis in Samples (ng/g)**

Isomer	Grain and Coffee samples	
	LOD (ng/g)	LOQ (ng/g)
$\alpha$ -HCH	0.05	0.2
$\beta$ -HCH	0.1	0.2
$\gamma$ -HCH(Lindane)	0.1	0.3
$\delta$ -HCH	0.1	0.2
HCB	1	3.5
Aldrin	0.1	0.4
Dieldrin	0.07	0.2
Endrin	0.08	0.3
Heptachlor	0.05	0.2
<i>Cis</i> -Heptach	0.06	0.2
<i>Trans</i> -Heptach	0.07	0.2
<i>Oxy</i> -chlordane	0.09	0.3
<i>Cis</i> -Chlordane	0.08	0.3
<i>Trans</i> -Chlordane	0.1	0.4
<i>Cis</i> -Nonachlore	0.1	0.3
<i>Trans</i> -Nonach	0.1	0.3
<i>o,p</i> -DDE	0.1	0.3
<i>p,p</i> -DDE	0.1	0.2
<i>o,p</i> -DDD	0.1	0.3
<i>p,p</i> -DDD	0.02	0.1
<i>o,p</i> -DDT	0.1	0.4
<i>p,p</i> -DDT	0.1	0.3
Mirex	0.1	0.2

LOD = Minimum limit of detection for the sample

LOQ = Minimum limit of quantification for the sample

**Recovery Analysis:**

The recovery ration of clean up spike was calculated according to the following formula.

$$Rc = (Acsi/Arsi) \times (Qrsi/RRFr) \times (100/Qcsi)$$

Where, Rc = Recovery ratio of clean up spike (%)

Acsi = peak area of internal standard substance for cleanup spike

Arsi = peak area of corresponding internal standard substance for syringe spike

Qrsi = Added amount of corresponding internal standard substance for syringe up spike (ng)

RRFr = Relative response factor of corresponding internal standard substance for syringe spike

Qcsi = Added amount of internal standard substance for cleanup spike (ng)

**Recovery Result for OCPs Analyzed in Green Coffee Bean:**

The mean recovery and standard deviation of OCPs compounds analyzed in green coffee ranged from 59% - 96 % and 5 – 19 % respectively. While, the recovery and standard deviation of OCPs compounds analyzed in blank test for green coffee beans analysis ranged from 58% - 110 % and 4 - 24 % respectively as shown on table 4. However, the mean recovery ratio of HCB was almost zero. So that, the concentration level of HCB in green coffee bean was not reported (not analyzed).

**Table 4: The Mean Recovery and Standard Deviation of POPs Analyzed in Green Coffee Beans**

POPs	Coffee Blank (n=3)		Sample( n=11)	
	Recovery (%)	STD (%)	Recovery (%)	STD (%)
$\alpha$ -HCH	71	18	76	8
$\beta$ -HCH	109	5	83	11



$\gamma$ -HCH(Lindane)	87	12	84	7
$\delta$ -HCH	90	10	78	8
HCB	-	-	55	20
Aldrin	58	15	61	5
Dieldrin	71	5	68	5
Endrin	73	11	96	19
Heptachlor	104	24	95	16
<i>Cis</i> -Heptachlor epoxide	98	14	87	8
<i>Trans</i> -Heptachlor ep.	98	14	87	8
Oxychlordane	83	7	85	9
<i>Cis</i> -Chlordane	91	4	78	7
<i>Trans</i> -Chlordane	91	4	78	7
<i>Cis</i> -Nonachlor	93	7	72	11
<i>Trans</i> -Nonachlor	93	4	74	4
<i>o,p'</i> -DDE	91	10	74	7
<i>p,p'</i> -DDE	84	4	59	6
<i>o,p'</i> -DDD	110	7	82	9
<i>p,p'</i> -DDD	105	7	84	12
<i>o,p'</i> -DDT	98	12	85	11
<i>p,p'</i> -DDT	89	9	76	8
Mirex	89	4	83	11

### 3. RESULTS AND DISCUSSION

A summary of the organochlorine pesticides residues concentration levels in green coffee samples is shown in Table 5. While,  $\Sigma$ HCH [ $\alpha$ -HCH,  $\beta$ -HCH,  $\delta$ -HCH],  $\Sigma$ Aldrin, heptachlor (*Cis*- and *Trans*-heptachlor epoxide), Endrin,  $\Sigma$ Chlordane (sum of *oxy*-chlordane, *cis*-Chlordane, *cis*- and *trans*-Nonachlor), and Mirex were not detected in all of green coffee beans. HCB was not analyzed.

Gamma-HCH in five, heptachlor in two, *trans*-chlordane in two, *o,p'*-DDE in three, *p,p'*-DDE in three, *o,p'*-DDD, *p,p'*-DDD in one, *o,p'*-DDT in one and *p,p'*-DDT in one coffee samples were detected at BQL. Gamma-HCH and heptachlor were detected only in one of coffee sample from Addis Ababa city with the concentration of 1.21ng/g and 0.301ng/g, respectively. DDT and their metabolites were detected in most of coffee samples ranged 0.062ng/g to 51.7ng/g. *Para, para'*-DDT isomer was the dominant contaminant in green coffee beans as shown in Figure 10.

According to JMH (Japan Ministry of health, Labor and welfare) report, some of coffee bean imported to Japan from Ethiopia had pesticides ( $\gamma$ -HCH, Chlordane, DDT, and Heptachlor) over MRLs of Japanese especially in 2008 [11].

In this study, the concentration levels of other OCPs in green coffee beans were found at far below when compared to the JMH MRLs except DDT. However, the  $\Sigma$ DDT concentrations ranged 0.014ppm – 0.075ppm in six samples were exceed the MRL established by Japanese (0.01ppm).

**Table 5: Concentration Levels of OCPs in Green Coffee Beans**

POPs Isomers	Concentration(ng/g) in Green Coffee Samples											
	Place Samples	Nekemte					Addis Ababa		Jimma			
		1	2	3	4	5	6	7	8	9	10	11
$\alpha$ -HCH		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
$\beta$ -HCH		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
$\gamma$ -HCH(Lindane)		BQL	ND	ND	ND	BQL	BQL	1.2	BQL	ND	BQL	ND
$\delta$ -HCH		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
HCB		NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Aldrin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Dieldrin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Endrin		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Heptachlor		BQL	ND	ND	ND	ND	ND	0.399	ND	BQL	ND	ND
<i>Cis</i> -Heptach		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Trans</i> -Heptachlor		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
Oxychlordane		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Cis</i> -Chlordan		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Trans</i> -Chlord		ND	ND	ND	ND	BQL	ND	BQL	ND	ND	ND	ND

<i>Cis</i> -Nonach	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>Trans</i> -Nonach	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
<i>o,p'</i> -DDE	ND	ND	BQL	ND	ND	ND	BQL	ND	ND	ND	BQL
<i>p,p'</i> -DDE	BQL	0.215	1.95	BQL	0.225	0.775	0.924	0.516	0.709	BQL	2.33
<i>o,p'</i> -DDD	ND	0.476	1.78	ND	BQL	BQL	0.765	BQL	0.335	ND	1.03
<i>p,p'</i> -DDD	0.149	1.98	8.19	BQL	0.771	1.22	2.19	0.477	1.59	0.062	4.80
<i>o,p'</i> -DDT	BQL	2.76	10.4	ND	1.35	2.05	4.30	0.684	3.33	ND	5.58
<i>p,p'</i> -DDT	0.568	8.82	51.7	BQL	4.92	11.0	8.98	2.11	10.44	BQL	21.5
Mirex	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Where, ND = Not detected, BQL = below quantification limit, NA = Not analyzed

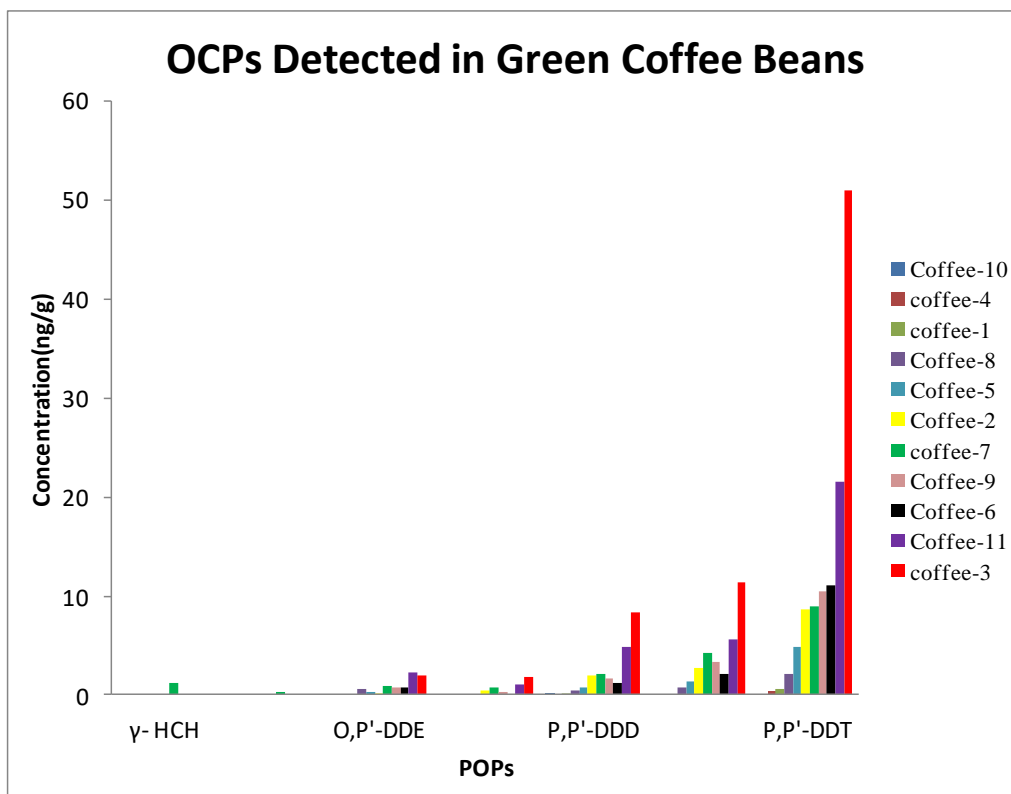


Figure 2: Concentration Levels of Organochlorine Pesticides in Green Coffee Beans

#### Estimation of Daily Intake (EDI) of DDT from Coffee Produced in Ethiopia:

To determine the potential risk of pesticide residues, the intake of DDT from coffee consumption was estimated and compared with Acceptable Daily Intakes (ADI) mentioned by WHO/FAO. The daily intake of DDT via coffee was calculated as follows.

DDT daily intake = DDT conc. x average coffee bean daily intake/ person body weight /day

- DDT concentrations (mg/kg): maximum residue of DDT in coffee beans in this study (0.075 mg/kg),
- Average coffee intake (g)/day: assume average daily intake per day of coffee in Ethiopia (5 grams per person/day), and
- Person body weight (kg) = 60 kg.

$$\begin{aligned} \text{DDT daily intake} &= 0.075 \text{ mg/kg} \times 0.005 \text{ kg} / 60 \text{ kg /day} \\ &= 6.25 \text{ ng/kg body weight/day} \end{aligned}$$

The ADI of DDT by FAO/WHO (20  $\mu\text{g/kg}$  body weight/day) [12]. The estimated daily intake of DDTs via coffee intake by human was far below the allowable daily intake recommended by FAO/WHO, showing that the intake of DDTs would not pose health risk in Ethiopia.



#### 4. CONCLUSION AND RECOMMENDATION

##### 4.1. Conclusion:

Ethiopia is a country whose half of GDP is lie on agricultural products. It is the birthplace of coffee Arabica. It was 5<sup>th</sup> coffee producer and 8<sup>th</sup> exporter in 2007. The use of pesticide is increasing worldwide, and particularly among rural populations of the developing world whose economy relies mostly in agriculture. Thus, contamination of the environment with pesticides and the pesticides entry into the food chain is unavoidable especially in developing countries. According to some reports, highly imports and inappropriate use in Ethiopia are warranted because of absence of effective controlling mechanisms for pesticides. Unfortunately, Ethiopian coffee imported to Japan had pesticides (Heptachlor, Lindane, Chlordane and DDT) contaminations problem in 2008. Therefore, the aim of this study was to investigate current pesticides concentration levels in foodstuffs from Oromia, Ethiopia.

A study was conducted to investigate persistent organic pollutants (POPs) residue levels in coffee beans, grain and fish food commodities from Oromia region, Ethiopia. These samples were randomly collected from local markets from four cities during May to June 2011, while fish samples were taken immediately from Lake Ziway.

HRGC/HRMS was used for the determination of 23 organochlorine pesticides compounds in all samples. The extraction and clean up were done based on QuEChERS methods with slightly modification. Total PCBs was measured in fish muscle by using HRGC/HRMS after extraction was done by alkali saponification and clean-up with multilayer silica gel. The accuracy of the analytical methods of POPs and PCBs were confirmed by using reference materials. Therefore, analysis of POPs and PCBs were conducted for foodstuffs under the condition of high quality control and quality assurance.

ΣAldrin (Aldrin and Dieldrin), heptachlor (*Cis*- and *Trans*-heptachlor epoxide), Endrin, ΣChlordane (Oxychlordane, *Cis*-Chlordane, *Cis*- and *Trans*-Nonachlor), HCH ( $\alpha$ -HCH,  $\beta$ -HCH and  $\delta$ -HCH) and Mirex were not detected in all food samples. However, DDT was highest contaminants among OCPs analyzed in all food samples, especially in green coffee, from Oromia, Ethiopia. These indicate DDT was used in the past and still in use. Thus, there is DDT pollution problem in the environment in the country.

Interestingly, our research found PCB IUPAC-#11 dominantly though a little environmental burden by commercial PCBs in Ethiopia. Our finding results obtained in this study provide vital information for the control and address further significance of researches on OCPs and PCBs in Ethiopia.

##### 4.2. Recommendation:

Our findings suggest a need to investigate the state of organochlorine pesticides in the environment and their effects on wildlife and human health. Especially, further detailed studies on DDT regarding environmental pollution should be performed. Moreover, this study shown these food items are contaminated with five organochlorine pesticides so it is clear that consumption of foods containing unsafe amount of pesticide residues are of public health concern, consequently demanding additional health cost. In addition to these, it may affect economic value especially for export products. Thus, all concerned bodies of the country need to play their crucial role for providing safe foods and ensuring public health by continuing monitoring by increasing number of foodstuffs, target compound of pesticides in use today and expanding monitoring regions in Ethiopia are necessary.

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