



Research article

Organochlorine pesticide residues in tea and their potential risks to consumers in Ethiopia

Jafer Siraj^{*}*School of Pharmacy, College of Medicine and Health Sciences, Mizan-Tepi University, Mizan-Aman, Ethiopia*

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ABSTRACT

Tea is the most frequently consumed drink in the sphere; next to the water. However, tea can be contaminated by different pesticides particularly those outdated pesticides which have been familiar as one of the main difficulties in Ethiopia and contaminate the food commodities. From a study done in south west of Ethiopia, Dichlorodiphenyltrichloroethane (DDT) and endosulfan were detected in commonly consumed food items. Therefore, the main aim of this study was to analyze the residue of organochlorine pesticides (OCPs) in tea collected from the market and assessing their risks to consumers. 19 different tea samples were randomly collected from supermarkets in Jimma town and Addis Ababa city. In the analytical procedure, QuEChERS (Quick, Easy, Cheap, Rugged, and Safe) method was applied for the extraction of tea samples. The finding of the study revealed that, five OCPs (aldrin, γ -chlordane, DDT, endrin, and dibutylchloroepoxide) were detected at a concentration of 0.1465, 0.167, 0.2044, 0.3067 and 0.4089 mg kg⁻¹ in domestic tea, respectively, while endosulfan sulfate, methoxychlor, and heptachlor epoxide were detected at a concentration of 0.258, 0.458 and 1.427 mg kg⁻¹ in imported tea samples respectively. From the pesticides detected, the mean concentration of DDT (0.292–0.825 mg kg⁻¹) is above the Maximum Residue Limits (MRLs) established by China (0.2 mg kg⁻¹). The estimated daily intake (EDI) of γ -chlordane and endrin were above the acceptable daily intakes (ADIs), this indicates that there is a health risk for tea consumers. The detection of pesticide residues in tea reveals that there is the widespread use of OCPs in the study area for agricultural purposes or as vector control. Therefore, strict regulation of pesticides during production, importing, sale, and application in the field is important for Ethiopia.

1. Introduction

Pesticide use is a central practice in the agriculture to enhance the quantity of food produced for the fast population growth and for the prevention of vector borne diseases. Thus, the environmental effect of pesticides and the accumulation of pesticides in food chain are inevitable particularly in emerging nations. Organochlorines enter in to the food chain and bioaccumulate in adipose tissue due to their lipophilic nature and persist in the ecosystems for a long duration [1]. The pesticides used in farmland and crop productions are varied from dangerous complexes like organochlorine pesticides (OCPs) to less toxicity. Organochlorine substances are less dissolved in aqueous solution, little polarization capacity, highly dissolved in lipid, become concentrated inside the bodies of living things (bioaccumulate), ability to transport far-off and persist in the ecosystems [2,3]. Many of the organochlorine compounds are considered as persistent organic pollutants (POPs) because of their ability to persist in the ecosystems for a extended duration once they used for

crop production or vector control and this was the reason why organochlorine pesticides especially POPs banned by United Nations Environment Program [4].

Tea is the most frequently consumed drink in the universe, next to water and recognized as one of the most popular healthy drink for consumers in 21st century. Tea plant is a crop that harvested multiple times annually, therefore, the intervals between the pesticide application and tea plucking is shorter than other crops and the tea fresh leaves are directly manufactured after plucking and without washing [5]. Pesticides have been used during the production of tea to enhance the quantity of tea produced through controlling pest. Therefore, numerous pesticides residues are frequently identified in raw tea and processed tea [6,7]. Consequently, tea users' awareness has been boosted, and the quality and safety of tea has developed a widespread concern. So, pesticide residue in tea has currently become the highest issues to tea users. Chemicals play a significant part in the struggles of countries to realize economic advance and fulfill their development objectives [8]. However, as far as pesticides are

^{*} Corresponding author.

E-mail addresses: sirajjafer@gmail.com, jafersiraj@mtu.edu.et.

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essential for guaranteeing food security and economic development, improper and unselective use can be terrible both for public wellbeing and the ecosystems. In this situation, chemicals can have a dual characteristics; they can be either useful or risky, based on several factors, for instance the quantities to which exposure happens [9].

Recently, the incidence of harmful pesticides in the surroundings has become a concern of great discussion. Pesticides and other external elements in foodstuffs and drinking water pose an abrupt risk to public health and progressively persist in the ecosystems and in the human tissues, producing illness long after initial exposure [10]. In an industrialized countries, various old, non-patented, globally persistent, and cheap kinds of substances are used widely, which can able to cause significant health problems and environmental contamination [11]. According to FDA data from 2008 to 2012 on pesticide residues in tea (black, green, and oolong) reveals a high rate of violations and from the total tea samples examined, approximately 30 % have contaminated with two or more banned pesticides [12].

From a study done in India on pesticide residues, almost 94 % of the tea samples analyzed are contaminated with minimum one of 34 different pesticides studied, whereas more than half of the samples are contaminated with a toxic cocktail of more than 10 different pesticides [13]. Widespread contamination of tea plants with pesticides has also been reported in China [14]. Tea farming has increased majorly over the past decade globally [12]. In Ethiopia, tea production increased 15 to 7,400 tons from the year 1976 until 2013, respectively [15]. Even though, the use of chlorinated and persistent pesticides is restricted to indoor spraying for prevention vector-borne disease in Ethiopia, and there will be problem of contamination as the country has the largest accumulations of outdated pesticides in Africa. According to [16], about 3000 tons of hazardous pesticides dumped on nearly 1000 sites in Ethiopia and threatening the environment as well as human health. Also a study conducted in south west of Ethiopia showed that banned pesticides like p,p'-DDT, p,p'-DDE and endosulfan were identified in commonly consumed food items [17].

Studies focused on pesticide residues are highly required in order to estimate the level of contamination and at the same time to evaluate the effects of chemicals use during farming on consumer health. In Ethiopia, there is no study done particularly on the level of organochlorine pesticides in tea and their potential risks to consumers. Further, for the improvement of controlling strategies regarding pesticide inputs in farming with the target to develop safe and sustainable agronomic practices detail study is important. Thus, the main objective of this study was to investigate the residue of organochlorine pesticides in different brands of tea available in Ethiopian market and its potential risks to consumers.

2. Materials and methods

2.1. Sampling

A total of nineteen (19) commonly available tea brands collected from shops/markets found in Jimma and Addis Ababa cities. Out of these tea samples, fourteen brands were domestic and the remaining five were imported products. Each tea brand was collected from three different shops/markets and then mixed and homogenized before extraction (composite before extraction). In total, fifty-seven (57) tea samples were collected for the determination of organochlorine pesticides. Tea samples, containing green tea and black tea, were obtained from shops/local markets. The tea samples were processed, placed and closed in sterile polyethylene bags and written off as with distinctive sample characteristics.

2.2. Chemicals and reagents

All organic solvents proposed for extraction, were HPLC (High Performance Liquid Chromatography) grade and bought from different local suppliers and importers found in Ethiopia (Table 1). Nine organochlorine

pesticides standard manufactured by PIPARK Scientific Limited, Northampton, UK were purchased from local suppliers and have analytical standard grade more than 97.9 %. The standards include; DDT, dielderin, endrin, γ -Chlordane, Endosulfan Sulfate, Aldrin, Heptachlorepoxide (Isomer B), Dibutylchlorepoxide, and Metoxychlor.

2.3. Sample preparation, extraction and cleanup

Extraction and clean-up of the spiked samples and blank samples from each matrix were done by means of modified QuEChERS method. Samples of dried and homogenized tea leaves (2 g) were weighed into 50 ml centrifuged tubes and left to hydrate for 30 min after the adding 10 ml of distilled water and agitated by hand for 30 s. Acetonitrile (10 ml) was then added and the tubes shaken by hand dynamically for 1 min. Magnesium sulphate (4 g) and sodium chloride (1 g) salts were added to remove water from the samples. After more vigorous shaking for 1 min, the samples were centrifuged using a Model PLC 02, Taiwan Inc. USA for 5 min at 10,000 rpm. A 1 ml of supernatant organic layer was then removed to 15 ml centrifuged tube. Then 1ml n-hexane and 5 ml of 20 % w/w aqueous sodium chloride solution was added. The tube was agitated vigorously for 1 min and then centrifuged for 1 min at 10,000 rpm. An aliquot of the upper organic layer was removed to vial for injection. Each sample was replicated three times to get reliable results according to [18]. Finally, the extracted samples were inserted into gas chromatography with electron captured detector and the types, and amounts of organochlorine residues were investigated.

2.4. Chromatographic analysis

The determination of the pesticides under study was carried out using Gas Chromatography with an Electron Capture Detector (GC-ECD, Agilent Technologies 7890A). An HP-5 capillary column (30 m \times 0.25 mm inner diameter; 0.25 μ m film thickness) coated with 5 % phenyl methyl siloxane (model 19091J-433; Agilent) was used in combination with the following oven temperature program: initial temperature of 80 $^{\circ}$ C, ramped at 30 $^{\circ}$ C min^{-1} to 180 $^{\circ}$ C, ramped at 3 $^{\circ}$ C min^{-1} to 205 $^{\circ}$ C, held for 4 min, ramped at 20 $^{\circ}$ C min^{-1} to 290 $^{\circ}$ C, held for 8 min, ramped at 50 $^{\circ}$ C min^{-1} to 325 $^{\circ}$ C. The total GC run time was 27.92 min. Nitrogen (99.9999 % purity) was used as a carrier gas at a flow rate of 20 mLmin^{-1} and as makeup gas at a flow rate of 60 mLmin^{-1} . An aliquot of 1 mL was injected in split less mode and injection temperature of 280 $^{\circ}$ C. The pesticide residues were detected with μ -ECD detector operating at a temperature of 300 $^{\circ}$ C. The tea samples were analyzed in triplicate and the mean concentration was computed accordingly.

The retention times of the peaks of the sample chromatogram obtained were compared to the retention time of the corresponding peaks in the standard curves. The sample equivalent (mgmL^{-1}) extract was calculated based on the formula suggested by [19].

$$Y = \frac{a}{b} \times \frac{x}{z}$$

Where:

Y is grams of sample equivalent per milliliter of extract,
a is the amount of sample analyzed (g),
b is the volume of solvent added to extract the sample (mL),
x is the amount of the cleaned extract taken for GC analysis (mL), and
z is the amount of hexane added for solvent exchange (mL).

2.5. Quality assurance and quality control

2.5.1. Linearity of the standard curves

All the calibration curves showed linearity for all the pesticides of interest with the coefficient determination, $r^2 > 0.999$ which is in the acceptable analytical range according to SANCO [20].

Table 1. Description of chemicals and reagents.

Chemical	Purity	Manufacturer/Supplier
n-hexane	99 % for HPLC	Carlo Erba reagents
Acetonitrile	99.9 % for HPLC	LobaChemie PVT, Ltd., Mumbai, India
Magnesium sulphate	99 % Laboratory reagent	Central drug house (P) LTD., New Delhi, India
Sodium chloride	99.5 % Laboratory reagent	Tachnopharmchem, Bahadurgarh, India
Methanol	≥99.9 % for HPLC	Sigma Aldrich. Co, Germany.

2.5.2. Limits of detection and limits of quantification

Limits of detection (LOD) and limits of quantification (LOQ) of the method was measured in by spiked serial dilution of working standards prepared for calibration curves and calculated by considering a value 3 and 10 times of background noise, respectively. The concentration of OCPs identified from the each tea samples were compared using limit of detection by considering the evidence that the other literatures also presented in similar way [5,17].

2.5.3. Recovery studies

To determine the accuracy of the methods, recovery study of the pesticides were undertaken. Pesticides under study were spiked in blank tea samples at concentration levels of 1mg l^{-1} and then treated as per to the sample preparation method. The recoveries were considered by means of the peak areas from calibration curves and obtained from the spiked samples. Also, a blank analysis was performed as per to the sample preparation method to determine possible interference from the sample [21]. The detected concentration in blank analyses is below the LOD.

2.6. Data analysis

The outputs generated from the chromatographic study were summarized by means of descriptive statistics (mean \pm standard deviation). Descriptive statistics was determined along with the one way ANOVA via SPSS (Version 21). All the mean values of OCP residues were compared with maximum pesticides residual limits in food samples established by Codex alimentary, European Union standards and China.

2.7. Health risk assessment

To assess the toxicological significance of human exposure to the pesticide residues present in tea, it is essential to determine the Estimated Daily Intake (EDI) and compared with the Acceptable Daily Intakes (ADI) proven by FAO/WHO. ADI is the amount of the pesticides taken daily without any appreciable risk through the entire lifetime [22]. Human health risk assessments were conducted depending on the pesticide residue data base and tea consumption assumptions per capita per year, and by considering 60 kg as average body weight of Ethiopian People. The annual tea consumption is 0.058 kg/capita/year for Ethiopia [23]. Results gotten were used to compute EDI and stated as $\mu\text{g/kg}$ body weight/day. The EDI is a accurate estimate of pesticide exposure that was calculated for each pesticide on tea in covenant with the universal standards [24], using the following equation:

$$EDI = \sum C \times \frac{F}{D} \times W$$

Where:

- C is the mean concentration of the pesticide in tea (μgkg^{-1}),
- F is mean annual intake of tea per person,
- D is number of days in a year (365), and
- W is mean body weight (60 kg)

The chronic health risk was assessed by means of the hazard index (HI), this was calculated by dividing estimated daily intake (EDI) by the acceptable daily intakes (ADI) values as follow [25];

$$HI = \frac{\text{Estimated Daily Intake } (\mu\text{gkg}^{-1}\text{d}^{-1})}{\text{Acceptable Daily Intakes } (\mu\text{gkg}^{-1}\text{d}^{-1})}$$

3. Results and discussion

3.1. Method validation results

The percentage recoveries of the organochlorine pesticides were found to be 75.87 %–111.56 %, which is in the analytical acceptable range (70–120) (Table 2). This indicates the method is accurate. Pesticides residue analysis in foodstuffs by the QuEChERS technique is an ability to produce sound recoveries than the traditional methods of liquid-liquid extraction [20]. The LOD and LOQ varied from 0.06–0.72 and 0.3–2.4 μgkg^{-1} , respectively. The coefficient of determination for all the pesticides studied were in the acceptable analytical range ($r^2 > 0.999$) [20]. The RSD for all the pesticides investigated were lower than 9 % which is consistent with the normally recognized level which is $<20\%$ [19].

3.2. Residues of organochlorine pesticides

From the findings of the present study, aldrin was detected in 13 (92.86 %) domestic tea samples at a concentration of between 0.260 to 0.896 mgkg^{-1} whereas only detected in two (40 %) imported tea samples at a concentration of 0.385 and 0.58 mgkg^{-1} (Table 3). This may be due to the application in the agricultural fields or the historical use of these pesticides for malaria control in Ethiopia. The persistent nature of organochlorine pesticides in the environment from the previous applications in agricultural and public health is also another reason for their presence in tea samples [3]. The bioaccumulation levels of these organochlorine pesticides in plant tissues are greater than those in ambient environmental media such as air and water. These activities lead to the entrance of organochlorine pesticides in to food chain like tea plants [25]. The present result was similar with the study conducted in south-west Ethiopia in which Aldrin was identified from cereal crops obtained from the study area [17]. High mean concentration of heptachlorepoide residue was detected in both domestic tea (1.242mgkg^{-1}) and imported tea (1.08mgkg^{-1}) samples. Generally, the mean concentrations of this organochlorine pesticide residue (heptachlorepoide) were varied from 0.107mgkg^{-1} to 1.242mgkg^{-1} and from 0.618mgkg^{-1} to 1.08mgkg^{-1} in domestic tea samples and imported tea samples (Table 3), respectively. This may be probably due to the contamination of the tea samples during transportation or storage to supermarkets and shops. The present finding was much lower than the results reported from Pakistan which reported that the detected concentrations of DDTs and HCHs are ranged between $2.23\text{--}24.9\text{ ng g}^{-1}$ and $0.44\text{--}10.3\text{ ng g}^{-1}$, respectively [26].

From the total domestic tea samples ($n = 14$) analyzed in this study, about 13 (92.86 %) of the tea samples were contaminated with aldrin, heptachlorepoide, chlordane and p,p-DDT pesticide residues. Whereas seven pesticide residues including aldrin, heptachlorepoide, chlordane p,p-DDT, endosulfan, dieldrin and methoxychlor were detected in two (40 %) imported tea samples. The result of the present study showed

Table 2. The percentage recoveries and validation information of the studied organochlorine pesticides standard.

Pesticides	Recovery (%)	RSD	LOD (mgkg ⁻¹)	LOQ (mgkg ⁻¹)
Aldrin	95.57	3.6	0.10	0.34
Dibutylchloroepoxide	89.67	1.7	0.16	0.54
γ-Chlordane	111.56	0.9	0.72	2.40
DDT	102.45	8.3	0.14	0.48
Endrin	75.87	9.0	0.15	0.50
Endosulfan Sulfate	87.23	1.3	0.15	0.50
Dieldrin	78.90	5.8	0.06	0.30
Methoxychlor	82.13	0.8	0.15	0.50
Heptachlorepoide	99.24	6.2	0.15	0.50

RSD is relative standard deviation; LOD is limit of detection; LOQ is limit of quantification; DDT is dichlorodiphenyltrichloroethane.

Table 3. Mean concentrations of the OCPs in different brands of tea samples in Ethiopia and comparisons with MRLs.

Samples	Category	Mean Pesticide Concentration (mgkg ⁻¹) (Mean ± SD)									
		Aldrin	Heptachlorepoide	γ-Chlordane	p,p-DDT	Endrin	Endosulfan sulfate	Dieldrin	Methoxychlor	Dibutylchloride	
Brand A	Domestic	0.260 ± 0.011	0.362 ± 0.029	0.449 ± 0.078	0.633 ± 0.015	0.384 ± 0.023	< LOD	< LOD	< LOD	< LOD	
Brand B	Domestic	0.468 ± 0.083	0.279 ± 0.098	0.440 ± 0.081	0.338 ± 0.011	0.342 ± 0.054	< LOD	< LOD	0.598 ± 0.065	0.718 ± 0.050	
Brand C	Domestic	0.896 ± 0.081	0.275 ± 0.010	0.416 ± 0.034	0.292 ± 0.025	0.546 ± 0.056	0.435 ± 0.094	0.228 ± 0.010	0.226 ± 0.088	0.727 ± 0.024	
Brand D	Domestic	0.55 ± .023	0.648 ± 0.075	0.413 ± 0.030	0.356 ± 0.058	0.322 ± 0.091	0.461 ± 0.080	0.182 ± 0.053	< LOD	< LOD	
Brand E	Domestic	0.598 ± 0.016	1.242 ± 0.038	0.575 ± 0.068	0.392 ± 0.028	<LOD	< LOD	0.409 ± 0.027	0.564 ± 0.026	0.517 ± 0.073	
Brand F	Domestic	0.809 ± 0.028	0.489 ± 0.018	0.592 ± 0.018	0.351 ± 0.023	<LOD	< LOD	0.557 ± 0.019	0.589 ± 0.056	0.568 ± 0.097	
Brand G	Domestic	0.893 ± 0.051	0.107 ± 0.044	0.428 ± 0.039	0.407 ± 0.038	<LOD	< LOD	0.423 ± 0.029	< LOD	< LOD	
Brand H	Domestic	0.28 ± 0.042	0.799 ± 0.020	0.264 ± 0.079	0.736 ± 0.084	0.347 ± 0.045	< LOD	0.271 ± 0.034	< LOD	< LOD	
Brand I	Domestic	0.599 ± 0.094	0.704 ± 0.043	0.658 ± 0.019	0.697 ± 0.035	0.694 ± 0.071	0.688 ± 0.039	0.478 ± 0.015	< LOD	< LOD	
Brand J	Domestic	0.288 ± 0.005	0.559 ± 0.015	0.336 ± 0.019	0.394 ± 0.002	0.358 ± 0.001	1.060 ± 0.01	0.676 ± 0.05	0.731 ± 0.057	0.859 ± 0.018	
Brand K	Domestic	0.794 ± 0.015	0.573 ± 0.015	0.286 ± 0.05	0.757 ± 0.05	0.280 ± 0.05	< LOD	0.190 ± 0.001	0.467 ± 0.088	0.558 ± 0.027	
Brand L	Domestic	0.368 ± 0.02	0.648 ± 0.090	0.456 ± 0.090	0.641 ± 0.015	0.149 ± 0.022	0.464 ± 0.008	0.544 ± 0.01	< LOD	0.464 ± 0.01	
Brand M	Domestic	0.602 ± 0.05	0.331 ± 0.05	0.186 ± 0.008	0.825 ± 0.00	0.538 ± 0.004	< LOD	0.141 ± 0.025	0.484 ± 0.014	< LOD	
Brand N	Domestic	<LOD	< LOD	< LOD	< LOD	<LOD	< LOD	< LOD	< LOD	< LOD	
Brand O	Imported	0.385 ± 0.084	1.08 ± 0.029	0.542 ± 0.084	0.691 ± 0.024	0.337 ± 0.057	0.143 ± 0.018	0.374 ± 0.042	0.395 ± 0.060	< LOD	
Brand P	Imported	0.58 ± 0.068	0.618 ± 0.011	0.618 ± 0.040	0.637 ± 0.061	< LOD	0.361 ± 0.097	0.394 ± 0.044	0.430 ± 0.047	0.633 ± 0.016	
Brand Q	Imported	<LOD	< LOD	< LOD	< LOD	<LOD	< LOD	< LOD	< LOD	< LOD	
Brand R	Imported	<LOD	< LOD	< LOD	< LOD	<LOD	< LOD	< LOD	< LOD	< LOD	
Brand S	Imported	<LOD	< LOD	< LOD	< LOD	<LOD	< LOD	< LOD	< LOD	< LOD	
MRLs (mgkg ⁻¹)	Codex	NE	NE	NE	NE	NE	10	NE	NE	NE	
	China	NE	NE	NE	0.2	NE	10	NE	NE	NE	
	EU	NE	NE	NE	NE	NE	30	NE	NE	NE	

Key: NE is Not Established; LOD is Limits of Detection; MRLs is Maximum Residue Limits.

higher detection of pesticides than the study done in Iran which reported that out of fifty three tea samples only 28.3 % of the samples contaminated with pesticides [21] and lower than the result reported from china in which 198 samples (88.8 %) are contaminated with different concentrations level of residues [5]. Also, from the analysis of previous available FDA data on residue concentrations in tea from 2008 to 2012 reveals that out of the 65 samples of tea, approximately 30 % had two or more banned residues which is lesser than the result obtained in the present study [12]. This difference could be due to the fact that in Ethiopia there is a high potential are in agricultural and there is a probability of OCP use in the past for vector control for public health issues [27]. An additional reason could be bleaching and surface run-off of pesticides due to the presence of dumped obsolete pesticides in more than 1000 sites in Ethiopia [28].

In this study, DDT was identified in the both domestic and imported tea samples which also related with the study done in India that showed DDT residues found, which has been banned for use for agriculture since

1989 [13]. Also, similar result reported from Pakistan that showed DDTs were found to be the leading isomer of organochlorine pesticides in rice straw samples [26]. Also, another study from China reported that pyrethroids have been preferred usually and extensively in tea farming to avoid and regulate various tea pests for the reason that they have immediate action and poisonous to pests at minimum amounts and have a lethal effect [29]. The other organochlorine pesticide endosulfan sulfate was detected in 35.71 % of domestic and 40 % of imported tea samples which is higher than the result reported from Iran which is 18.9 % of samples contaminated with endosulfan sulfate [21]. The difference could be attributed to variations in geographic settings, the study conducted at different period and the degree of former use of these organochlorine pesticides. Even though several countries have been banned or severely controlled the usage of most hazardous organochlorine pesticides, it is assumed that lots of these chemicals have been used in huge amounts in some emerging tropical nations for farming and human health reasons as control of diseases, such as malaria [27].

Table 4. Estimated Daily Intakes (EDIs) and Hazard Index (HI) of pesticide residues detected in domestic or imported tea.

Samples	Category	γ -Chlordane			p,p-DDT			Endrin			Endosulfan sulfate		
		ADI ^a ($\mu\text{gkg}^{-1} \text{d}^{-1}$)	EDI ($\mu\text{gkg}^{-1} \text{d}^{-1}$)	Hazard index	ADI ^a ($\mu\text{gkg}^{-1} \text{d}^{-1}$)	EDI ($\mu\text{gkg}^{-1} \text{d}^{-1}$)	Hazard index	ADI ^a ($\mu\text{gkg}^{-1} \text{d}^{-1}$)	EDI ($\mu\text{gkg}^{-1} \text{d}^{-1}$)	Hazard index	ADI ^a ($\mu\text{gkg}^{-1} \text{d}^{-1}$)	EDI ($\mu\text{gkg}^{-1} \text{d}^{-1}$)	Hazard index
Brand A	Domestic	0.5	4.28	8.56	10	6.03	0.6	0.2	3.66	18.3	-	-	-
Brand B	Domestic	0.5	4.19	8.39	10	3.22	0.32	0.2	3.26	16.3	-	-	-
Brand C	Domestic	0.5	3.97	7.93	10	2.78	0.28	0.2	5.20	26.03	6	4.15	0.69
Brand D	Domestic	0.5	3.94	7.87	10	3.39	0.34	0.2	3.07	15.35	6	4.39	0.73
Brand E	Domestic	0.5	5.48	10.96	10	3.74	0.37	-	-	-	-	-	-
Brand F	Domestic	0.5	5.64	11.28	10	3.34	0.33	-	-	-	-	-	-
Brand G	Domestic	0.5	4.08	8.16	10	3.88	0.39	-	-	-	-	-	-
Brand H	Domestic	0.5	2.51	5.03	10	7.01	0.70	0.2	3.31	16.54	-	-	-
Brand I	Domestic	0.5	6.27	12.54	10	6.64	0.66	0.2	6.61	33.08	6	6.56	1.09
Brand J	Domestic	0.5	3.20	6.40	10	3.75	0.37	0.2	3.41	17.06	6	10.10	1.68
Brand K	Domestic	0.5	2.72	5.45	10	7.21	0.72	0.2	2.66	13.34	-	-	-
Brand L	Domestic	0.5	4.34	8.69	10	6.11	0.61	0.2	1.42	7.10	6	4.42	0.74
Brand M	Domestic	0.5	1.77	3.54	10	7.86	0.79	0.2	5.12	25.64	-	-	-
Brand N	Imported	0.5	5.16	10.33	10	6.58	0.66	0.2	3.21	16.06	6	1.36	0.23
Brand O	Imported	0.5	5.89	11.78	10	6.07	0.61	-	-	-	6	3.44	0.57

Key: ^a Established by Codex Alimentarius Commission; EDI is Estimated Daily Intake; ADI is Acceptable Daily Intake.

3.3. Comparison of the concentration of the pesticides detected with MRLs

Maximum residue limits (MRLs) reassure tea safety by limiting the amount of a residue allowed on tea, and the creation of MRLs is depends on good agricultural practice (GAP) data for teas. MRLs are not toxicological restrictions, but they must be toxicologically okay. Surpassed MRLs are good pointers of violations of GAP [30]. The comparison of the concentration of the pesticides detected in the present study with maximum residue limits (MRLs) set by EU, China and Codex Alimentarius indicated in Table 3. Most of the MRLs did not established for the organochlorine pesticides detected in this study by different international standards. Only one MRL for pesticide residue in tea was obtained from Codex Alimentarius standards [31], and European Union [32]. This may be due to; most of the organochlorine pesticides were banned from agricultural use in developed countries. According to Codex Alimentarius, DDT may be present in tea as a result of its presence as a contaminant in the technical dicifol [31]. The endosulfan Sulfate residue detected in tea samples was below the MRL established in both Codex Alimentarius and EU regulations. This indicates that there may be a good agricultural practice in the study area or may be because of the ban of OCPs from agricultural applications.

The average concentration of DDT is above the MRLs established by China [23] and indicates illegal use of this pesticide and similar result also obtained in the study done on commonly consumed food items in southwest, Ethiopia [17]. The level of DDT above MRL may be explained due to the historical use for malaria control or its persistent nature in the environment [33]. Even though the average concentration residues are above the standards, MRL does not indicate the toxicological effect it is necessary to check the risk of these pesticides to tea consumers by comparing with norm levels. The exposure of consumers is considered to be adequately known from pesticide risk, by calculating the daily intake and compared with the nom values acceptable daily intake (ADI). When the estimated dietary intake (EDI) of pesticide residues does not exceed the ADI, there is no risk and assures consumers safety.

3.4. Health risk assessment

Out of residues under the investigation, the acceptable daily intake (ADI) was established by Codex Alimentarius Commission for only four chemicals and accordingly, risk characterization was done for those chemicals. As indicated in Table 4, the estimated daily intakes of detected pesticides like DDT and endosulfan sulfate were lesser than ADIs, which

indicate that tea intake has an insignificant influence to toxicological risk for human being. In case of γ -chlordane and endrin, the estimated daily intakes were more than ADIs, which show that tea users are exposed to these two substances beyond the norm. Also, the estimated daily intakes of endosulfan sulfate were greater than ADIs in only two domestic tea samples. The user is considered to be effectively protected if the hazard index (HI) which is the ratio of EDI and ADI of a pesticide residue does not exceed one. The user is considered to be effectively endangered if the HI of a OCPs residue for a tea does not surpass one. If hazard index surpasses a value of one, this can show an intolerable health threat, so then the sources, pathways, and routes of pesticide introduction must to be assessed additionally [34,35]. The HI values showed that the intakes of γ -chlordane and endrin residues remains clearly above the norm value ($HI > 1$). There may be a health risk for tea consumers due to exposure to γ -chlordane and endrin through tea consumption.

Therefore, it can be decided that residues identified in teas are not predictable to create a human health threat. On the other hand, in sight of the number of positive results, controlling programs for these OCPs would be applied to confirm the lowest acceptable residue concentrations in teas. Stringent regulations on this pesticides and similarly additional monitoring would be emphasized that dietary pesticide exposures from other foodstuffs such as grains, vegetables, fruits, milk products, fish, and meats would be important and collective risk calculation would be conducted from cumulative intake. By itself, estimations are not taken as overall dietary exposure to the pesticides, nor do study drinking water, residential, or occupational exposures.

4. Conclusions

The findings from this study concerning to the detection of organochlorine pesticide residues in tea samples are probably a suggestion of the prevalent use in the study setting. From the total tea samples analyzed in this study, most of the tea samples were polluted with more than one organochlorine pesticide. Even though the residues were detected in many of domestic and imported tea samples, the mean concentration of all of the samples were below the MRLs set by EU and Codex Alimentarius. Organochlorine pesticide residues detected were also compared with MRLs established by China and only DDT was above the MRLs. This finding showed that there is illegal use of DDT in the study setting. The estimated daily intakes of γ -chlordane and endrin were greater than acceptable daily intake ($EDI > ADIs$), which show that tea consumers are highly exposed. The hazard index values showed that the

intake of γ -chlordane and endrin residues remains clearly above unity. The results showed that the risk related with exposure via tea intake is high; a special preventive measure must be taken with the potential total exposure to these substances from different foodstuffs in the future. Strict quality control at the border of importing tea is important for the safety of the people in Ethiopia. Tea processing like boiling may reduce the toxicity of the organochlorine pesticide residues in tea. So, further study on organochlorine pesticide residues in tea infusion should be important.

Declarations

Author contribution statement

Jafer Siraj: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Data availability statement

Data will be made available on request.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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