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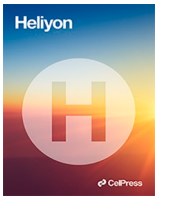

Research article

Levels of organochlorine pesticides in onion and tomato samples from selected towns of Jimma Zone, Ethiopia

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ABSTRACT

This study aimed to determine residues of organochlorine pesticides (OCPs) in tomato and onion samples collected from selected markets in the Jimma zone. A QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method was used for sample preparation followed by gas chromatography-mass spectrometry (GC-MS) for OCPs analysis. The method used showed wide linear ranges from 5-50 μg/L for all eight pesticides, with R^2 values $\geq$ 0.992. The LOD values for the pesticides tested ranged from 0.14 μg/kg for p,p'-DDE to 2.40 μg/kg for p,p-DDT. LOQ values ranged from 0.46 μg/kg for p,p-DDE to 8.32 μg/kg for p,p'-DDT. The recoveries ranged from 74.84 – 109.45 % except for β-BHC (67.82 %). While most of the OCPs in the onion and tomato samples met European Union (EU) and Codex standards, some exceeded the limits. Methoxychlor and p,p'-DDT in onions, and methoxychlor, p,p'-DDT, α-BHC, and δ-BHC in some tomatoes, were detected above the permitted levels. Specific OCPs were not detected in some samples including aldrin in Meki Tomato (Mek-T), γ-chlordane in Agaro Tomato (Ag-T), and p,p'-DDE in Gera Tomato (Ger-T). The residual concentrations of OCPs varied among the samples. Among tomatoes, Gera had the highest percentage of detected OCPs contaminants (37 %), followed by Agaro (34.34 %) and Meki (28.55 %). Similarly, Sire onion (SrO) had the highest percentage of detected OCPs (28 %) compared to Minjer (25.16 %), Shewa Robit (25.10 %), and Sudan onion (22.25 %). In conclusion, most tomato and onion samples analyzed in this study contained OCP residues highlighting the importance of conducting a consumer health risk assessment.

1. Introduction

Pesticides are chemical substances used to control, repel, attract, or eradicate pests such as weeds, insects, bacteria, and other nuisances [1]. They are classified into various categories, including organochlorines, organophosphates, carbamates, and pyrethroids. Different types of pesticides are applied globally across a wide range of crops to manage pest populations [2]. Agricultural productivity can be enhanced by applying pesticides such as herbicides, and fungicides to provide a sufficient food supply for the growing world population. It is important to note that after application to a target place, a small amount of pesticides remains in or on the crop after harvesting, making their way into the food chain [3]. Compared to other exposure routes, orally ingested pesticides have higher harmful effects. The use of these compounds gained prominence with the introduction of synthetic pesticides in the 1940s, particularly with the advent of organochlorine pesticides (OCPs) for pest control [4].

OCPs are a class of insecticides used to control insects in pre- and post-harvest crop management as well as to control vectors that

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cause malaria. These chemicals are categorized as persistent organic pollutants (POPs) due to their long-lasting nature, ability to accumulate in organisms, and lipid solubility [5]. Special attention has been given to these chemicals due to their toxicity and persistence in the environment. They pose serious and chronic health risks, including cancer, nerve damage, and disability in humans who are exposed to them. Although, several OCPs were banned from use in the United states and Europe several years ago, they are still in use in many developing countries due to their perceived effectiveness, and low cost [3,6].

Applying pesticides to crops during cultivation or post-harvest may leave residues that persist in the edible portions that are consumed by human beings [7]. This poses a series public health concern in regions where pesticides are extensively used on agricultural products such as fruit and vegetable production.

On the other hand, vegetables play a vital role in daily nutrition and are considered functional foods due to their beneficial biological compounds [8]. Tomatoes, for instance, are rich in vitamins, minerals, and carotenoids, particularly vitamin C, phosphorus, potassium, and lycopene, which gives them their red color [9,10]. They are a staple food in various Ethiopian regions like Walo, Hararge, Shawa, Jimma, and Wallaga [11]. Tomatoes are widely cultivated across Ethiopia, adapting to varying rainfall patterns ranging from 700 to over 1400 mm annually [12]. Onions were introduced to Ethiopia's agricultural landscape in the early 1970s by foreigners, marking their potential for year-round production both for local consumption and export [13]. However, challenges such as pests have significantly impacted vegetable production in Ethiopia, leading to the widespread use of pesticides as a remedy [14,15].

Various types of pesticides, including banned ones, are being excessively utilized in fruit and vegetable production across different districts of Ethiopia. For instance, over 40 % of farmers in the Gera district of Jimma zone use one or more agrochemicals and pesticides [16]. Additionally, approximately 24 % of farmers employ untrained daily laborers for pesticide spraying. A survey conducted by the Irrigation Development Authority Office in Ziway and Meki districts of the Central Rift Valley (CRV) of Ethiopia during the 2013/14 period revealed that 13,889 smallholder vegetable growers collectively used 53,044 L of pesticide and 50,957 kg of fungicide [16,17].

Various pre-treatment and extraction methodologies are utilized to analyze pesticide residues in fruits and vegetables [18]. Initially, liquid-liquid extraction (LLE) and solid phase extraction (SPE) were commonly used due to their simplicity. However, over the past decade, the QUEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method has gained significant attraction for its micro-scale extraction process. Moreover, owing to its substantial advantages in terms of simplicity, speed, selectivity, and flexibility, this technique has been officially recognized and adopted by the Association of Official Analytical Chemists (AOAC) [19].

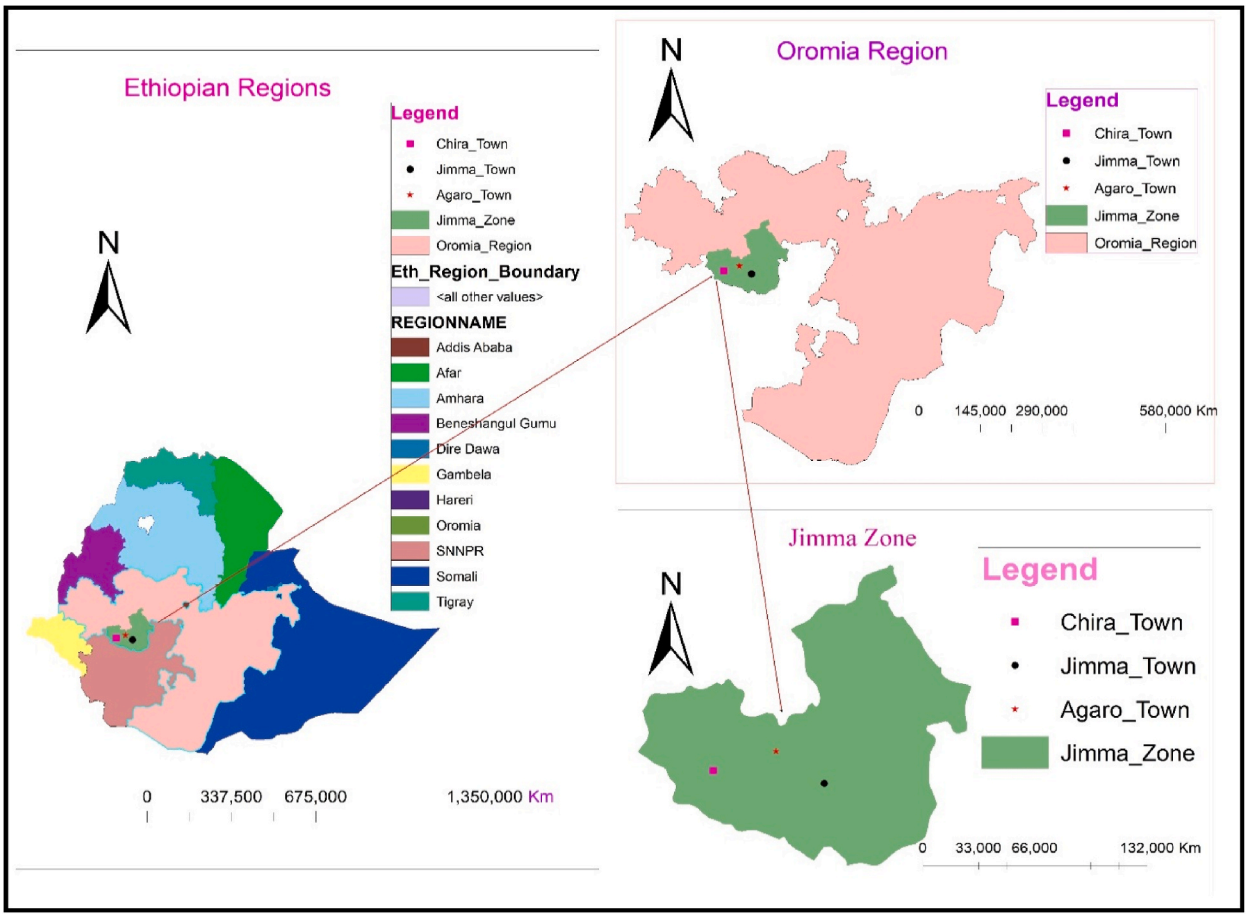

Fig. 1. Map of the study area.

Most vegetables sold in markets and super-markets contain pesticide residues due to the unregulated use of pesticides in cultivated fields, causing harmful effects on human health [20]. Previous studies have indicated the presence of certain OCPs in onion and tomato samples from specific locations within the Jimma zone [21,22]. However, these studies did not comprehensively assess all classes of OCP residues in these samples. Despite the widespread use of banned chemical pesticides in vegetable production in the Gera District [16], the earlier report on the Jimma zone did not address this issue. Therefore, the current study focuses on additional OCPs that were not considered in previous research. This investigation aimed to determine selected OCP residues in tomatoes and onions collected from open markets in selected towns within the Jimma zone, Ethiopia.

2. Materials and methods

2.1. Sampling site and sample collection and preservation

2.1.1. Sampling site

The study area was the open markets of selected towns in Jimma Zone, South-Western Ethiopia (Fig. 1). The three market places chosen were in Chira town of Gera Woreda, Agaro town of Gomma Woreda and Jimma town, located in different parts of Jimma Zone. These markets were selected purposively for sample collection based on their consumer purchasing capacity, pesticide usage status in the district, and the variety of vegetable products available.

2.1.2. Sample collection and preservation

First, market retailers and truck drivers who transport the vegetables from the farmland to the selected marketplace were interviewed about the origin of the vegetable samples. Based on the obtained information a total of 28 tomato and onion subsamples were collected from the three purposively selected vegetable markets to produce 7 representative samples. Sixteen subsamples of onions, which included four subsamples for each of the four different origins of onion samples (Shewa Robit, Minjer, Sire and Sudan) were collected to produce the four representative samples of onions from Jimma town.

On the other hand, twelve subsamples of tomatoes which included four subsamples for each of the three different origins for tomato samples (Meki, Gera and Agaro) were collected from the three market places (Chira Town, Agaro Town, and Jimma Town) to produce the three representative samples of tomatoes for each of the three different origins.

Depending on their origin, seven representative samples for both vegetable types (four different origins for onion and three different origins for tomato) were randomly collected. The subsamples were then combined to create one representative sample of 2 kg. The samples from each marketplace for both tomato and onion were separately sealed (based on their origin and type) in plastic bags, labeled, and then transported to Jimma University, Analytical Chemistry Laboratory. The collected samples were kept at 4 °C for subsequent OCPs analyses.

2.2. Chemicals and reagents

Acetonitrile (99.9 %) from CARLO-ERBA Reagents S.A.S (France) and n- Hexane (99 %) from LOBA Chemie PVT (India) were used as extraction solvents. Anhydrous reagent grade $MgSO_4$ and sodium chloride were supplied by BDH Chemicals Ltd. (Poole, England). Analytical grade standards, including Dichlorodiphenyltrichloroethane (DDT) (98.9 %), Dichlorodiphenyldichloro-ethylene (DDE) (99.9 %); chlorinated cyclodienes such as γ-chlordane (98.8 %); aldrin (≥98.8 %); methoxychlor (97.7 %); and Benzene Hexachlorides (BHC) including α-BHC (99.5 %), β-BHC (99.5 %), and δ-BHC (99.5 %) were obtained from Sigma Aldrich (St. Louis, MO, USA). Florisil with mesh size 60–100 (Merck, Germany) was used for their cleanup of the extract.

2.3. Preparation of standards

Initially, individual stock standard solutions were prepared at a concentration of 1000 mg/L and stored in a refrigerator at or below 4 °C. Subsequently, an intermediate standard solution of 100 μg/L was created by diluting a suitable volume of these stock solutions in hexane. All solutions were kept in the refrigerator at 4 °C. Fresh working solutions were then prepared by diluting the intermediate standard solution as required.

2.4. Sample preparation

Preparation of tomato and onion samples for pesticide analysis required meticulous attention to ensure precise and reliable results. Tomatoes were washed thoroughly with water to remove surface dirt and contaminants without damaging the skin. Similarly, the outer layers of onions were carefully peeled off. Each sample was then quartered using a stainless steel knife on a cutting board to aid in subsequent processing. The remaining portions were blended with an electric blender, ensuring the blender was washed thoroughly to prevent cross-contamination before its next use. Only the edible portions were used for analysis, with any bruised or rotten parts being diligently removed. These rigorous protocols maintained sample integrity and analysis accuracy. Finally, 10 g of the homogenized sample was extracted and subjected to cleanup processes [6].

2.5. Analytical procedure

2.5.1. Extraction

The modified QuEChERS sample extraction procedure was used in this study [6,21]. Each homogenized onion and tomato sample (10 g each) was separately placed into a 50 mL Falcon centrifuge tube. Then, 15 mL of acetonitrile was added, and the mixture was vigorously shaken for 1 min. A predetermined quantity of anhydrous magnesium sulfate and sodium chloride was added to the mixture, followed by shaking for 1 min and centrifugation at 5000 rpm for 5 min. The resulting supernatant was carefully transferred into a 15 mL centrifuge tube containing anhydrous $MgSO_4$ and florisil for further purification. After other round of shaking for 1 min and centrifugation at 5000 rpm for 5 min, 1 mL of the supernatant was transferred to a 100 mL round-bottomed flask, and the solvent was evaporated using a rotary evaporator under reduced pressure at 40 °C. Subsequently, 2 mL of n-hexane was added to the flask for solvent exchange. Finally, 1 μL of the extracted sample was injected into GC-MS for the analysis of OCP residues [23].

2.5.2. Instrumental analysis

The analysis of OCPs was conducted using an Agilent 8890 GC coupled with an Agilent 5977B single quadrupole Mass Spectrometer Detector (MSD) and an Agilent G4513A auto sampler (Agilent Technologies, USA) for sample injection into the gas chromatograph. An Agilent Technologies HP-5MS capillary column (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness) was employed for analyte separation. The MSD operated in time-scheduled selected ion monitoring (SIM) mode. High-purity helium (99.999 %) served as the carrier gas at a constant flow rate of 1.0 mL/min. The gas chromatograph functioned in split less mode. The temperature program for the GC was initiated at 100 °C, then increased at a rate of 15 °C/min to 200 °C, held for 5 min; raised at 4 °C/min to 250 °C, maintained for 4 min; and finally increased at 10 °C/min to 270 °C, held for 10 min. The injector port temperature was set at 280 °C. Operating parameters for the MSD in electron ionization mode included an ionization energy of 70 eV, GC-MSD transfer line temperature of 250 °C, ion source temperature of 230 °C, and quadrupole temperature of 150 °C. The scan range was set from 45 to 500 *m/z* with a scan time of 150 s per scan and a solvent delay time of 3 min [23].

2.6. Quality assurance (QA)

Quality of the method used was assured through a method validation that involves conducting experiments to confirm that a method can reliably produce accurate results within its intended scope [24]. In this study, accuracy and precision (% recovery and % RSD, respectively) were assessed through recovery experiments. This involved spiking a suitable volume of pesticide standards into onion and tomato samples in four replicates, each containing the same pesticide concentrations. The % RSD was calculated by dividing the standard deviation by the mean concentration and multiplying by 100. Percentage recovery (% R) was determined by dividing the concentration of recovered pesticide by the spiked concentration. The spiked samples were allowed to sit for 1 h before extraction to facilitate the partitioning of pesticides into the sample matrices [25].

Linearity was confirmed by constructing calibration curve for each analyte using six-point concentration levels ranging from 5.00 to 50.00 μg/L. Each concentration level was analyzed using GC-MS under defined chromatographic conditions.

2.6.1. Linearity study

The purpose of the linearity study was to verify the instrument's ability to produce accurate and reliable measurements over a certain range of concentrations. In this study, an external calibration curve was used to perform linearity study, using a six concentration points ranging from 5.00 to 50.00 μg/L. The calibration curve was then plotted as peak area versus concentration for each pesticide. The calibration curves of the eight OCPs exhibited satisfactory linearity with coefficients of determination, R^2, ranging from 0.992 to 0.998. The residual concentration of each pesticide in the tomato and onion samples was then determined using the calibration curve equation.

2.6.2. Limit of detection and quantification

The limit of detection (LOD) refers to the minimum detectable concentration of the analyte, at which precision and accuracy are deemed acceptable. Conversely, the limit of quantification (LOQ) is the minimum concentration of the analyte that can be accurately and precisely quantified. Both LOD and LOQ were determined from signal to noise ratio (S/N) as 3 and 10 times S/N (i.e., 3S/N and 10 S/N), respectively [22].

Table 1
Results of Linearity study with Calculated LOD (μg/kg) and LOQ (μg/kg).

Analyte	R^2	Linearity equation	LOD	LOQ
α- BHC	0.994	y = 20.095x - 51.4	0.19	0.62
β-BHC	0.994	y = 20.361x - 53.5	0.19	0.62
δ-BHC	0.997	y = 5.421x - 26.5	0.88	2.9
Aldrin	0.998	y = 6.669 x - 9.8	0.69	2.3
Methoxychlor	0.998	y = 15.791x - 91.4	0.36	1.2
γ-chlordane	0.995	y = 18.479x - 53.8	0.24	0.80
P,P′- DDE	0.992	y = 34.283x - 16.4	0.14	0.46
P,P′-DDT	0.996	y = 1.108 x - 3.5	2.4	8.3

In this study, the LOD values of the target pesticides ranged from 0.14 to 2.4 μg/kg, while the LOQ values ranged from 0.46 to 8.3 μg/kg. The LOD (0.14–2.4 μg/kg) and LOQ (0.46–8.3 μg/kg) values obtained in this study were lower compared to those reported by Barriada-Pereira et al. [26] which were LOD (0.70–8.5 μg/kg) and LOQ (6.3–44 μg/kg), respectively. In general, the obtained LOQ and LODs for both samples were below the maximum residue levels (MRL) established by the Codex and the European Union [21,22,27] indicating the feasibility of the method for analysis of the target OCPs residues in the onion and tomato samples. The linearity equation, R^2, LOD, and LOQ values are presented in Table 1.

2.6.3. Precision and recovery studies

The precision (repeatability) of the method was determined by extracting and analyzing target analytes in tomato and onion samples in replicates. The method's repeatability was evaluated using the relative standard deviation (%RSD). The %RSD values obtained for the analytes were consistently below 12 %. A lower %RSD is generally considered more desirable, as it indicates a higher degree of precision/repeatability.

The recovery study was performed by spiking onion or tomato samples with a known amount of the target pesticides and then, analyzed after extracting them from the samples using the modified QUECHERS method. For both tomato and onion samples the obtained recoveries were in the range of 70–120 % (Table 2), which is acceptable for food analysis [28]. Among the analytes, methoxychlor showed the lowest recovery values in onion (74.84 %) and tomato (64.21 %) samples. This may be due to its loss during sample preparation and analysis steps.

2.7. Statistical analysis

All the data were statistically evaluated by using Microsoft Excel 2010 software. A one-way ANOVA test was conducted with a significance level of $p < 0.05$ and $\alpha = 0.05$.

3. Results

Determination of the residual concentrations of pesticides in vegetables and other food samples is important because they can impact consumers' health. This study analyzed, the residual levels of eight OCPs in onion and tomato samples from selected local markets in the Jimma zone, Oromia Regional State, Ethiopia.

3.1. Organochlorine pesticide concentration in onion samples

Eight OCP residues, specifically α-BHC, β-BHC, δ-BHC, aldrin, methoxychlor, γ-chlordane, p,p′-DDT, and its metabolite (p,p′-DDE) were detected in the onion samples collected from different towns in Jimma zone (Table 3). The residual concentration of methoxychlor exceeded EU standards in all tomato samples from different locations (Minjer, Shewa Robit, Sudan, and Sire districts).

3.2. Concentration of OCPs in tomato samples

The results showed that all OCP residues were detected in the tomato samples considered, except for aldrin in Maki-T, γ-chlordane in Aga-T and p,p′-DDE in Ger-T (Table 4). OCPs including α-BHC, δ-BHC, methoxychlor, and p, p′-DDT were found above EU and/or CAC standards in some of the tomato samples of from various localities.

3.3. Distribution of OCPs residues in onion and tomato samples

The distribution of OCPs in the samples under study is an important metric because it provides information about the relative contribution of different OCPs to the overall OCP burden in the sample. This information can be used to identify the most significant OCP contaminants and inform targeted interventions to reduce OCP levels in the samples being studied. For instance, if a particular OCP is found to have a higher distribution in tomato samples; it suggests that this OCP may be a priority for reduction efforts.

Table 2
The percent recovery and precision of validated analytical methods.

Analytes	%Recovery in Onion Sample		%Recovery in Tomato Sample	
	%Recovery	RSD	%Recovery	RSD
α-BHC	77.23	11.90	85.00	12.24
β-BHC	67.82	9.320	103.1	8.900
δ-BHC	90.21	12.30	99.21	13.22
Aldrin	109.5	4.200	86.51	12.10
methoxychlor	74.84	9.650	64.21	5.600
γ-chlordane	99.41	8.070	104.1	1.810
p,p′-DDE	96.81	6.880	94.31	6.940
p,p′-DDT	104.8	9.840	82.40	11.40

Table 3
The concentration of OCPs (Mean ± SD) in the analyzed onion samples.

Analytes	Concentration(μg/kg) of OCPs in Samples of different Origins				**MRLs (μg/kg)** [21,22,29]	
	SHRO	SrO	MO	SuO	EU	CAC
α-BHC	6.73 ± 1.29	10.8 ± 2.96*	7.03 ± 1.98	5.64 ± 0.59	10.0	NA
β-BHC	5.86 ± 0.71	9.53 ± 1.42	6.36 ± 0.59	5.49 ± 0.32	10.0	NA
δ-BHC	7.20 ± 0.81	8.72 ± 1.28	7.89 ± 1.09	7.01 ± 0.78	10.0	NA
Aldrin	6.84 ± 0.47	6.00 ± 1.02	7.64 ± 0.19	5.72 ± 0.32	10.0	10.0
Methoxychlor	7.69 ± 0.58*	11.1 ± 1.22*	8.53 ± 1.23*	7.85 ± 0.76*	5.00	NA
γ-chlordane	6.02 ± 0.48	5.76 ± 1.48	5.20 ± 0.04	5.31 ± 0.27	10.0	10.0
p,p′-DDE	6.60 ± 0.94	7.53 ± 2.46	6.31 ± 0.79	5.80 ± 0.001	50.0	50.0
p,p′-DDT	9.81 ± 2.52	7.78 ± 1.35	10.5 ± 1.04*	9.60 ± 0.57	10.0	10.0

Where; SHRO (Shewa Robit Onion), SrO (Sire Onion), MO (Minjer Onion), SuO (Sudan Onion), MRLs (Maximum Residue Limit), EU (European Union), CAC (Codex Alimentarius Commission); The mean value with * shows noncompliant value with EU and CAC standards.

Table 4
The Concentration of OCPs (Mean ± SD) in the analyzed Tomato samples.

Analyte	Concentration(μg/kg) of OCPs in Samples of different Origins			MRL(μg/kg) [22,29,30]	
	Mek-T	Aga-T	Ger-T	CA	EU
α-BHC	5.99 ± 0.71	8.89 ± 0.24	10.6 ± 0.71*	NA	10.0
β-BHC	5.21 ± 0.30	7.75 ± 0.61	6.72 ± 1.72	NA	10.0
δ-BHC	8.76 ± 0.66	10.2 ± 1.60*	6.62 ± 0.58	NA	10.0
Aldrin	ND	3.76 ± 1.26	6.98 ± 1.08	50.0	5.00
Methoxychlor	9.41 ± 1.08	10.7 ± 0.98*	13.6 ± 1.20*	NA	10.0
γ- chlordane	5.72 ± 0.99	ND	3.13 ± 0.23	50.0	10.0
p,p′-DDE	5.61 ± 0.27	6.29 ± 1.76	ND	NA	50.0
p,p′-DDT	8.89 ± 0.13	12.1 ± 0.72*	16.8 ± 0.63*	100.0	10.0

Where; Mek-T (Meki Tomato), Aga-T (Agaro Tomato), Ger-T (Gera Tomato), SD (Standard Deviation), ND (Not detected); NA (Not Available), the mean value with * shows noncompliant values with EU and CAC standards.

Additionally, this information can be used to inform the selection of pesticides for use in tomato production and to develop targeted pest management strategies.

Equation (1) is used to calculate the percentage distribution of each organochlorine pesticide in the detected sample relative to the total concentration of detected OCPs

$$\text{Percentage distribution} = \frac{\text{Concentration of individual OCP detected}}{\text{Total concentration of all detected OCPs}} \times 100 \quad (1)$$

3.3.1. Distribution of OCPs in tomato samples

The percentage distribution of OCPs in a tomato sample was calculated using Equation (1) above. Fig. 2 displays the percentage distribution of OCPs in each of the three tomato samples relative to the total OCPs detected. p,p′-DDT was the most commonly detected OCP in all samples, while its metabolite p,p′-DDE was lower compared to the parent compound. This suggests that there was recent use of p,p′-DDT [25,31]. Among the detected BHC compounds, ***α***-BHC was the most detected OCP in all tomato samples. Methoxychlor was the next most commonly detected OCPs followed by p,p′-DDT and α-BHC in Gera tomato. γ-chlordane (4.850 %) was the least detected OCP followed by δ-BHC (10.27 %) and β-BHC (10.40 %) in Gera tomato relative to the total OCPs.

3.3.2. Distribution of OCPs in onion samples

The percentage distribution of OCPs in onion samples was calculated using Equation (1). Fig. 3 shows the percentage distribution of OCPs in each of the four onion samples relative to the total detected. p,p′-DDT and its metabolite p,p′-DDE are the most common OCP detected, making up 29.37 % in Sudan onion (SuO), 28.97 % in Shewa Robit Onion (SHRO), and 28.41 % in Minjer onion (MO) of the total OCPs detected. The three BHCs (alpha, beta, and delta) together make up 34.60 % in SuO, 43.16 % in SrO, 34.66 % in SHRO and 34.41 % in MO relative to the total OCPs detected. γ-chlordane is the least detected OCP in all samples. Methoxychlor is the second most commonly detected OCP after p,p′-DDT OCPs in Sudan, Shewa Robit, and Minjer onion, respectively.

3.4. Comparison of OCPs residues in onion and tomato samples from different localities

The percentage abundance of all detected OCPs in samples from four different localities determined. This was done to provide a comparison and clear image of the relative proportions of detected pesticides in samples from varying localities. This allows for easy identification of the most prevalent pesticides and facilitates comparison of pesticides abundance across different sample origins.

In this study, "percentage abundance" refers to the proportion of the total concentration of OCPs contributed by each specific sample origin. It' serves as measure of the relative contribution of each origin to the overall OCPs load. The percentage abundance for

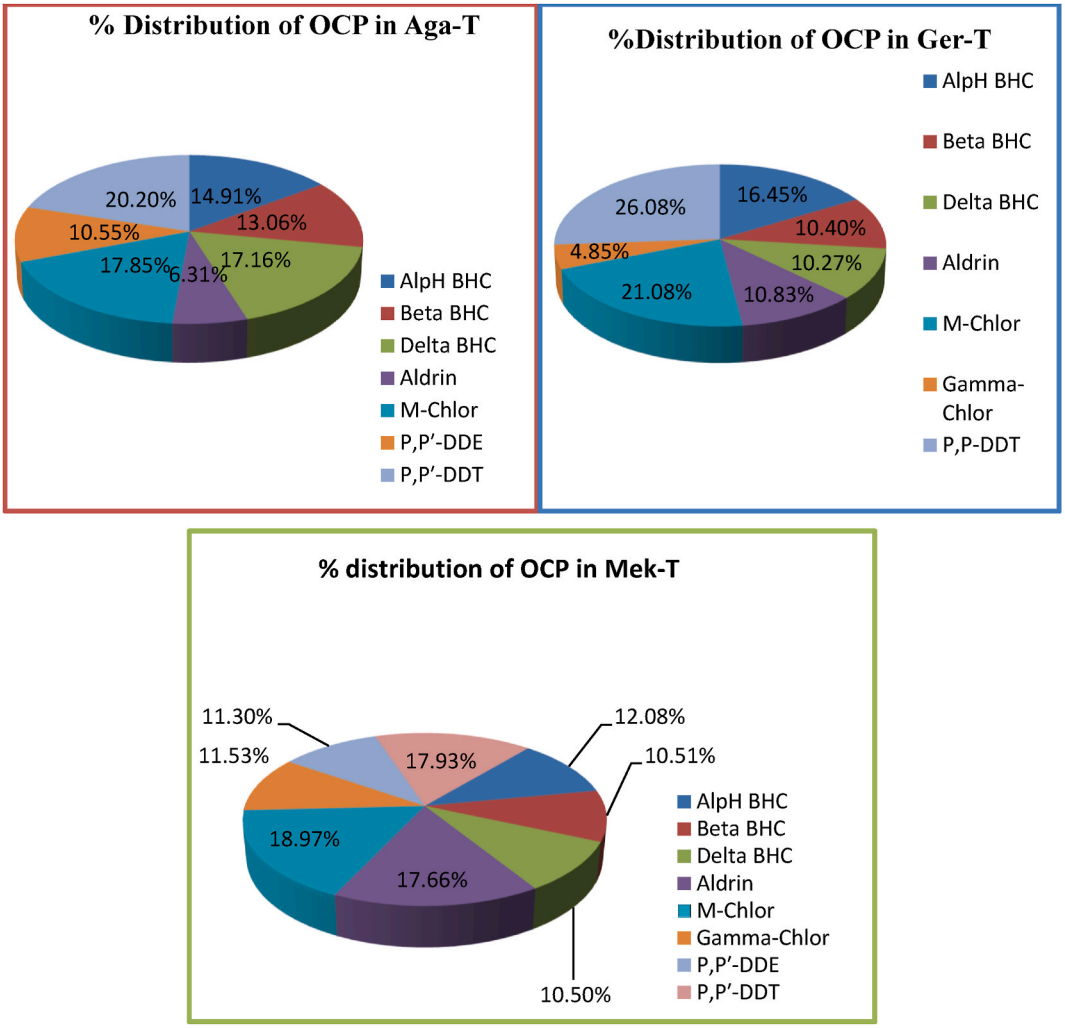

Fig. 2. Percentage distribution of OCPs in tomato samples.

each sample origin was calculated using Equation (2).

$$\text{Percentage abundance} = \frac{\text{Total OCPs concentration for origin } i}{\text{Total OCPs concentration for all origins}} \times 100 \tag{2}$$

where.

- i is the index of the sample origin (e.g., 1 for Shewa Robit onions, 2 for Sudan onions, etc.)
- Total OCPs concentration for origin i is the total OCPs concentration from that specific origin
- Total OCPs concentration for all origins is the total OCPs concentration from all origins

3.4.1. Abundance of OCPs residues in onion samples from different locations

The percentage abundance of all detected OCPs in onion samples from four different origins was calculated using equation (2). The finding showed that the highest percentage of detected OCPs was found in Sire onion samples, followed by Minjer, Shewa Robit and Sudan onion samples (Fig. 4). This indicates that Sire onions may have been exposed to higher levels of OCP contaminants than the others. This could be attributed to the historical use of OCPs being more common in Sire than in the other areas where the onions were grown [32]. Another possibility is that the Sire onions were transported or stored in a way that facilitated contamination with OCPs. Additionally, the contamination could also be a result of the disposal of outdated pesticides containing OCPs, such as DDT, in substantial quantities [31].

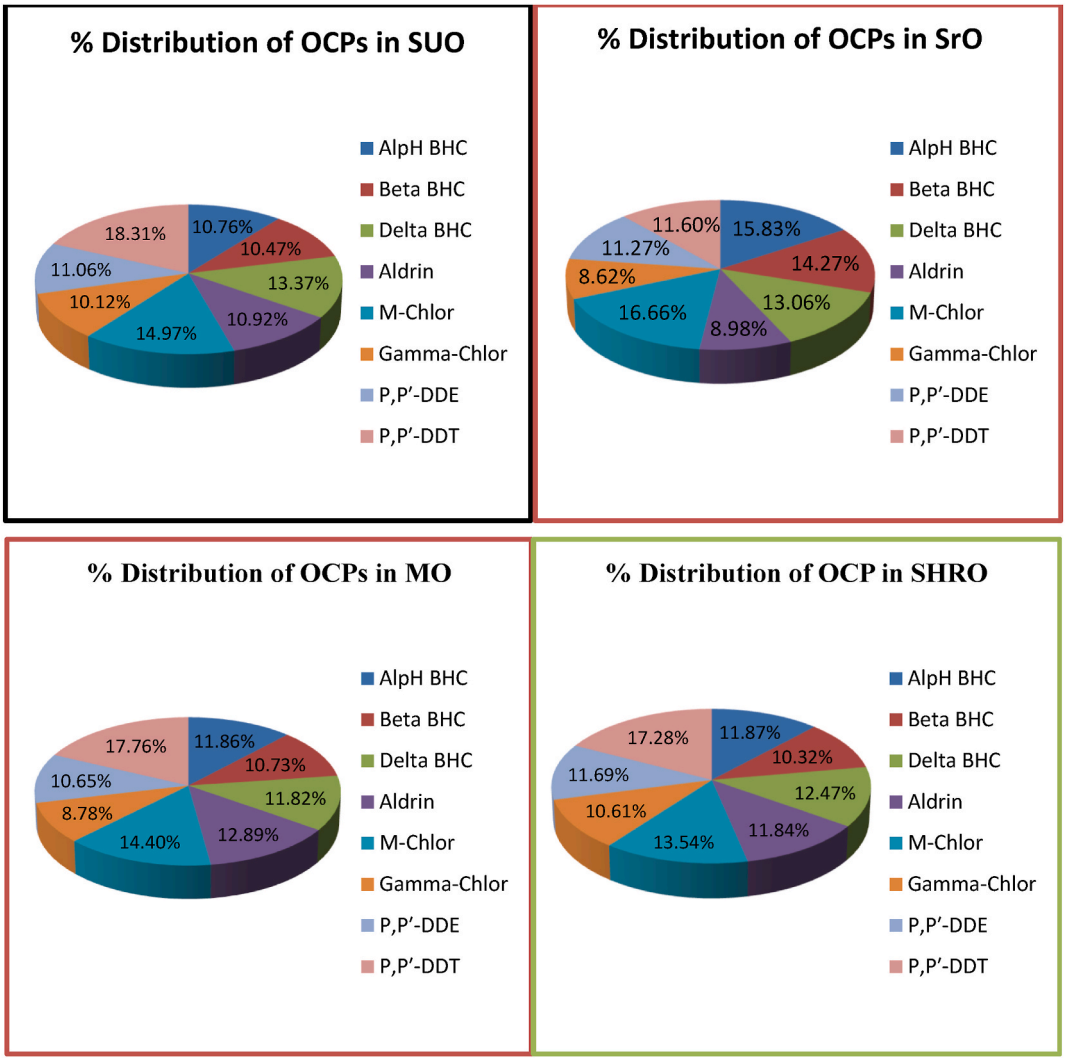

Fig. 3. Percentage distribution of OCPs in onion samples.

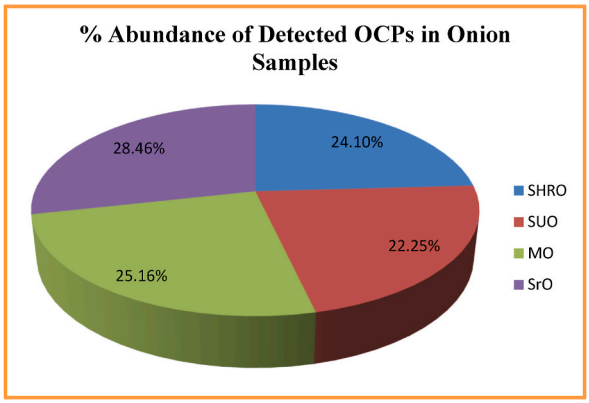

Fig. 4. Percentage abundance of OCPs in onion samples.

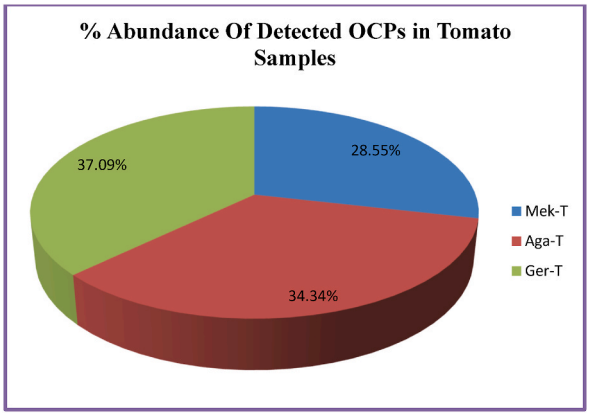

Fig. 5. Percentage abundance of OCPs in tomato samples.

3.4.2. Abundance of OCPs residues in tomato samples from different locations

The percentage abundance of detected OCPs in tomato samples from three different origins was determined using Equation (2). Fig. 5 illustrates that the highest percentage of OCPs was detected in Gera tomatoes, followed by Agaro, and Meki tomato samples. This implies that Gera tomatoes may have been historically exposed to higher contaminants OCPs compared to the samples of other origins. It suggests that improper use of OCPs was more prevalent in Gera than in other regions. Another indication is that the Gera tomato samples may have been transported or stored in a manner that facilitated contamination with OCPs [16].

4. Discussion

Residues of all eight Organochlorine Pesticides (OCPs) were detected in onion samples, and most OCPs were also found in tomato samples. The levels of OCP residues in the onion samples analyzed in this research were similar to those reported in previous studies. For instance, studies conducted in Ethiopia and Turkey by Kumelachew et al. [33] and Ozcan et al. [34], respectively, demonstrated comparable findings, as shown in Table 5. The findings of this investigation revealed that the concentrations of OCPs in onion and tomato samples collected from selected towns in the Jimma Zone of Ethiopia were generally higher than those reported in other countries, with a few exceptions. Notably, the levels of p,p'-DDE, p,p'-DDT, and aldrin in onions and tomatoes in this study were lower compared to those documented in Ghana [35]. Furthermore, the levels of p,p'-DDT in onions from this study were lower than those reported in Senegal [36].

Several factors may be contributing to the higher levels of OCPs found in tomato and onion samples in this study compared to other countries. For example, Ethiopia's regulations for pesticide use are less strict than those of other countries [37], resulting in a greater of OCPs in agriculture. Additionally, agricultural practices in Ethiopia may rely more on traditional pest control methods that involve the use of OCPs. Inadequate post-harvest handling and storage practices could also be contributing to the elevated levels of OCP in the tomato and onion samples in this study [16,38].

The presence of pesticide residues in vegetables and fruits is a widespread phenomenon worldwide. Table 3 details the concentration levels of pesticide residues detected in onion samples, as well as their maximum residue levels. The range of pesticide levels varies from the lowest concentration of γ-chlordane (5.20 ± 0.04 μg/kg) in Minger onion to the highest concentration of methoxychlor (11.1 ± 1.22 μg/kg) in Sire onion. Among the onion samples, Minjer onion had the highest mean concentration of 7.03 μg/kg for α-BCH residue, while Sudan onion also had the lowest mean concentration of α-BCH (5.64 μg/kg). Minjer onion also had the highest mean concentration of β-BHC residue (6.36 μg/kg), while Sudan onion had the lowest mean concentration of β-BCH (5.49 μg/kg). Shewa-robit onion had the highest mean concentration of δ-BHC residue (7.20 μg/kg), while Sudan onion had lowest mean concentration (7.01 μg/kg). The levels of $\boldsymbol{\alpha}$-BHC were found to be higher than $\boldsymbol{\beta}$-BHC in all samples, indicating recent introductions of new technical BHC or limited degradation. However, these findings contradict those reported by John et al. [29], where $\boldsymbol{\alpha}$-BHC and $\boldsymbol{\beta}$-BHC were not identified in any onion samples from markets in Dar es Salaam, Tanzania.

Similar to the study reported by Ozcan [34], there were variations in the occurrence of OCPs residues among the types of samples. The highest mean concentration of p, p′-DDT was found in all onion samples. All detected pesticides were below the EU and CAC MRLs except for methoxychlor and p, p'-DDT. Levels of OCPs in some products may be unexpected and h require further analysis and research. Minimum residual concentrations of aldrin and methoxychlor were reported in Sudan onion and Shewa-Robit onion at 5.72 μg/kg and 7.69 μg/kg, respectively. Similarly, minimum residual concentrations of γ-chlordane and aldrin were recorded in Sudan onion samples at concentrations of 5.31 μg/kg and 5.72 μg/kg, respectively. However, the minimum residual concentration of detected OCPs does not guarantee safety for human consumption. Therefore, frequent regulation, training of farmers on pesticide usage and the use of integrated pest management are crucial [37,39].

The concentration of pesticide residues detected in the examined tomato samples and their corresponding maximum residue levels were detailed in Table 4.The levels of OCPs in tomato samples range from ND in aldrin in Meki tomato, γ-chlordane of Agaro tomato, and p, p'-DDE in Gera tomato to the highest concentration of DDT (16.8 ± 0.63 μg/kg) in Gera tomato. The concentrations of detected

Table 5
Comparison of OCPs concentration in tomato and onion samples from Ethiopia and other counties.

Country	OCPs Residue	Concentration (μg/kg)	Food type	Reference
Turkey	α-BHC	3.84 ± 0.01	Onion	[34]
	β-BHC	ND		
	Methoxychlor	5.87 ± 0.05		
	δ-BHC	3.97 ± 0.02		
	4,4'-DDE	1.22 ± 0.09	Tomato	
	Aldrin	1.29 ± 0.02		
	4,4'-DDT	1.64 ± 0.03		
Ghana	Methoxychlor	4.00 ± 0.002	Tomato	[35]
	p,p'-DDE	13.0 ± 0.009		
	p,p'-DDT	12.0 ± 0.006		
	Aldrin	6.00 ± 0.002	Onion	
	p,p'-DDT	35.0 ± 0.005		
Ethiopia	4,4′-DDE	ND - 3.20	tomato	[33]
	4,4′-DDT	ND - 7.60		
	Methoxychlor	1.71 ± 0.02–2.88 ± 0.10	Tomato	[22]
	p,p'-DDE	1.20 ± 0.02–1.33 ± 0.01		
Senegal	DDT	12 ± 0.027	Tomato	[36]
	Aldrin	ND		
Ethiopia	α-BHC	5.64 ± 0.59–10.6 ± 0.70	Tomato and Onion	Current study
	β-BHC	5.49 ± 0.32–9.53 ± 1.42		
	Methoxychlor	7.69 ± 0.58–1 3.6 ± 1.20		
	δ-BHC	6.62 ± 0.57–10.2 ± 1.60		
	p,p'-DDE	ND - 7.53 ± 2.46		
	p,p'-DDT	7.78 ± 1.35–16.9 ± 0.63		
	Aldrin	ND - 7.64 ± 0.188		

ND: Not detected.

pesticides varied depending on the origin of the tomato samples. Meki tomato samples had the highest concentrations of methoxychlor (9.41 ± 1.08 μg/kg), δ-BHC (8.76 ± 0.66 μg/kg, and p,p'-DDT(8.89 ± 0.13 μg/kg), while Gera samples had the highest concentrations of methoxychlor and γ-chlordane. Agaro samples had intermediate concentrations of all pesticides. While the detected levels of contaminants are often below permissible limits set by the EU and CA, concerns remain about some samples exceeding the maximum residue levels (MRLs) for methoxychlor (all onion), p,p'-DDT(Ag-T and Ger-T), α-BHC (Ger-T) and δ-BHC (Ag-T). Further research is needed to identify the source of these OCPs and evaluate the potential health risks associated with their consumption.

In this study, one-way ANOVA was employed to assess whether there is a notable difference between the mean pesticide concentrations in the four onion groups and the three tomato groups based on their origin. The groups were based on the location where the onion was grown. The ANOVA test results indicate that among the detected OCPs in onion samples, four of them, namely α-BCH, δ-BHC, p,p'-DDE, and γ-chlordane, exhibited a significance level with $P \geq 0.05$, suggesting no significant difference among the tested groups (onions from four different origins). This indicates that there were no notable variations in the application or contamination trends of the pesticides. It's possible that onions from these four sources share similar abilities to absorb or accumulate pesticides [29]. In contrast, four of the tested OCPs, including p,p'-DDT, aldrin, methoxychlor, and β-BHC, showed p-values lower than the significance level of 0.05. This suggested that there was a noteworthy difference among the examined groups of onions from the four origins. For the tested OCPs in tomato samples, aldrin and methoxychlor exhibited $P \geq 0.05$, suggesting that there was no significant difference among the tested groups of tomatoes from three different origins.

4.1. Limitation of the study

The aim of this study was to analyze the residual concentration of OCPs in onion and tomato samples from selected towns of the Jimma zone. Although eight different organochlorine pesticides were analyzed, additional pesticides could be present in the samples that were not included in the study. Another limitation of the study could be that no health risk assessment was performed. The presence of pesticide residues in foods such as onions and tomatoes raises concerns about potential health effects on consumers that could have been assessed through a risk assessment.

5. Conclusion

The present study examined the levels of eight OCPs in onion and tomato samples in a selected town in the Jimma Zone, Oromia Regional State, Ethiopia. The OCPs in the samples were extracted using a modified QuEChERS method, followed by their determination using GC-MS analysis. The method's linearity ($R^2 > 0.992$), % recovery (70–120 %), and low values LOD and LOQ were appropriate, demonstrating its robustness for OCP analysis in tomato and onion samples. Analysis of the eight target OCPs in onion and tomato samples revealed their ubiquitous presence with intriguing variations in distribution and levels. α-BHC, β-BHC, aldrin, γ-chlordane, and δ-BHC were detected at lower levels, indicating less common usage in the area where the onions and tomatoes were grown. Conversely, methoxychlor, p,p'-DDE, and p,p'-DDT were detected above EU and CAC permissible limits in some samples, with

their higher levels suggesting potential persistence or recent application. Among tomatoes, Gera samples emerged as the champions of OCP accumulation, boasting a 37.1 % burden, followed by Agaro (34.3 %) and Meki (28.6 %). Therefore, further investigation into local agricultural practices and pesticide residue management in this area is crucial. The highest total OCPs detected in Sire onion compared to other districts is indication of either current or historical excessive usage of OCPs in the area. Overall, the results of this study revealed the presence of OCPs in onion and tomato samples collected from a selected town in the Jimma Zone. While the levels generally fall below the permissible standards set by CA and EU, they could still pose health risks to consumers. Certain OCPs have been associated with various health issues, such as cancer, reproductive disorders, and developmental abnormalities. Therefore, conducting a health risk assessment of the detected OCP residues in tomato and onion samples from this study is important.

CRediT authorship contribution statement

Umeta Jirata: Writing – original draft, Software, Investigation, Formal analysis. **Tsegaye Girma Asere:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Yerosan Buzayo:** Software, Investigation, Data curation. **Abera Gure:** Writing – review & editing, Validation, Supervision, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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