Bull. Chem. Soc. Ethiop. **2023**, 37(1), 23-33.
DOI: https://dx.doi.org/10.4314/bcse.v37i1.3

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

DETERMINATION OF ORGANOCHLORINE AND ORGANOPHOSPHORUS PESTICIDE RESIDUES IN TOMATO, POTATO, AND PINEAPPLE SAMPLES OF SELECTED FARMLANDS IN SOUTHWEST ETHIOPIA

Tamene Haile[1,3], Abera Gure[1*], Kassim Kedir[1] and Seblework Mekonen[2]

[1]Jimma University, College of Natural Science, Department of Chemistry, P. O. Box, 378, Jimma, Ethiopia
[2]Department of Environmental Health Science and Technology, Institute of Health, Jimma University, P. O. Box 378, Jimma, Ethiopia
[3]Parmanent address: Jimma Agricultural Research Center, Ethiopian Institute of Agricultural Research, P.O. Box: 192, Jimma, Ethiopia

(Received August 8, 2022; Revised August 31, 2022; Accepted August 31, 2022)

ABSTRACT. In this study, the residual concentrations of some organophosphate and organochlorine pesticides were determined in tomato, potato, and pineapple samples from selected farmlands of Jimma and Kefa Zones, Southwest of Ethiopia. The QuEChERS procedure, AOAC-2007, was used for extraction of the pesticides from the samples prior to their determinations by a gas GC-ECD. Pesticides including dichlorodiphenyltrichloroethane, endrin, and dieldrin were not detected in all studied samples. Dimethoate was detected only in Mana and Saka Buyo Qacama tomato samples. Likewise, malathion was detected only in the Saka Buyo Qacama tomato sample. The residual concentrations of most of the studied pesticides were below their MRLs set in EU guideline. However, the recorded residual concentrations of dibutyl chlorendate and chloroflurenol-methyl pesticides were above the EU general default MRL. The percent recoveries studied by spiking known concentrations of the analytes ranged from 71.22–121.56%. However, the recoveries of chloroflurenol-methyl and chlorpyrifos in the potato sample were 65.65 and 67.90%, respectively. One-way ANOVA results ($p \leq 0.05$) indicated the presence of significant variations in the concentrations of the detected pesticides among the sampling sites. Generally, the findings showed that regular monitoring of pesticide residues in agricultural products of the area is needed.

KEY WORDS: Organophosphates and organochlorines pesticides, QuEChERS, Tomato, potato, and pineapple samples, GC-ECD

INTRODUCTION

Pesticides are essential to kill and/or control pests that may cause the loss (ca. 40%) of the world agricultural production [1–3]. Annually, several million tons of pesticides are produced from about 1000 active substances against pests [4]. Unwise use of these pesticides can pollute the environment and food and thus, they can directly and/or indirectly harm the well-being of humans and other animals. Some pesticides are persistent against biological or chemical degradation and have a strong affinity to bioaccumulate in plants and animal tissues [5]. An earlier report revealed that each year, about 26 million people in the world suffer from pesticide poisoning [6]. From those pesticides, organophosphorus (OP) and organochlorine (OC) pesticides have been widely used for the control of insects and diseases from different agricultural crops including fruit and vegetables [7].

In Ethiopia, more than 85% of people's lives depend on agriculture. The sector is the dominant source of the nation's foreign currency earnings, sharing about 50% of its gross domestic product and 80% of the employment [8]. However, study findings showed that annually the country losses in an average 30 - 40% its crops due to pests. To reduce this loss the country has imported different types of pesticides to improve crop productions. Ethiopia had also been considered as the largest destination of obsolete pesticides in the horn of Africa [9].

*Corresponding author. E-mail: aberagure@gmail.com ; abera.gure@ju.edu.et

In Ethiopia, OC and OP pestcides have been used for long years to control insecticides from agricultural crops and for the control of malaria vectors [10, 11]. Residues of some OC pesticides were detected in teff, red pepper and coffee [12] and khat [13] collected from Jimma Zone, Ethiopia. These evidences clearly indicate the importance of determination of residues of OC and other pesticides in fruit and vegetable samples cultivated in the area to rescue the consumers. Therefore, this study was aimed to determine residues of some selected OP and OC pesticides in tomato, potato and pineapple samples cultivated in selected farmlands in Jimma and Kefa Zones in the Southwest of Ethiopia.

EXPERIMENTAL

Descriptions of the study area

The study was conducted in Jimma Zone from Oromia Reginal State and Kefa Zone from Southwest Ethipian Peoples Region State, both are located in the southwest of Ethiopia. Jimma Zone is located at latitude of 7°44' 59.99"N and longitude of 37°00'0.00"E and Kefa Zone is located at latitude of 7°20'15.00"N and longitude of 37°21'10.19"E. Totally, six Districts including Jimma Town (Amenu Kebele, and JARC), Shebe Sombo (Atrogefra Kebele), Saka (Buyo Qacama Kebele), Dedo (Waro Kolobo Kebele), Mana (Somodo Kebele) from Jimma Zone and Gojeb District (Horizon Plantation Private Limited Company, PLC) from Kafa Zone were considered in the study.

Sample collection

The samples were collected from April to May, 2018. Prior to the collection of samples, key informant interviews were conducted with farmers and agricultural extension experts of each District on the types and practices of pesticides use in their area, especially during cultivation of fruits and vegetables. Most of them replied that different pesticides such as malathion, diazinon, chloropyrifos, roundup, mancozeb, and others have usually been used in the area.

After getting this information, tomato, potato and pineapple samples were collected from three sites of the selected farmlands (1 kg/site) to form composite samples of 3 kg for each sample type. Similarly, blank tomato and potato samples were collected from Dedo District (Waro Kolobo Kebele) and pineapple samples were collected from Jimma Agriculture Research Center (JARC) experimental station plots. All blank samples were free from the target pesticides residues, confirmed by experimental studies. Then, the collected samples were transported to Jimma University Analytical Chemistry Laboratory and kept below 4 °C in a refrigerator until the time of sample preparation and subsequent analysis. Figure 1 shows map of the study area and the specific sampling sites.

Chemicals and reagents

All chemicals and reagents used were analytical grade and solvents were GC or HPLC grades. Organic solvents such as n-hexane was obtained from Lobachemiepvt. Ltd. (Mumbai, India) and acetone was purchased from Carlo Erba reagents S.A.S. (Mumbai, India). Glacial acetic acid was obtained from Blulux international PLtd (Stockholm, Malmo, Malmohus). Anhydrous magnesium sulfate ($MgSO_4$) and anhydrous sodium acetate (CH_3COONa) were supplied by BDH Chemicals Ltd (Poole, England).

Analytical grade standards of dichlorodiphenyltrichloroethane (p'p–DDT), dichlorodiphenyl-dichloroethylene (p'p-DDE), endosulfan sulfate, endrin, dieldrin, methoxychlor, dibutyl chlorendate (DBC), dimethoate, malathion, chloropyrifos, and chloroflurenol-methyl (chlorof-m) were obtained from Sigma Aldrich (St. Louis, MO USA). Individual stock standard solutions containing 1000 mg/L were prepared by dissolving appropriate weight of the pesticide standard

in methanol, with the exception of dimethoate, chloropyrifos, malathion and chlorof-m which were dissolved in acetonitrile. An intermediate standard solution containing a mixture of the target pesticides was prepared by diluting appropriate volumes of the stock standard solution of each analyte in acetone. All the prepared solutions were stored in the refrigerator at 4 °C. Working standard solutions were then prepared from the intermediate standard solution by diluting in n-hexane.

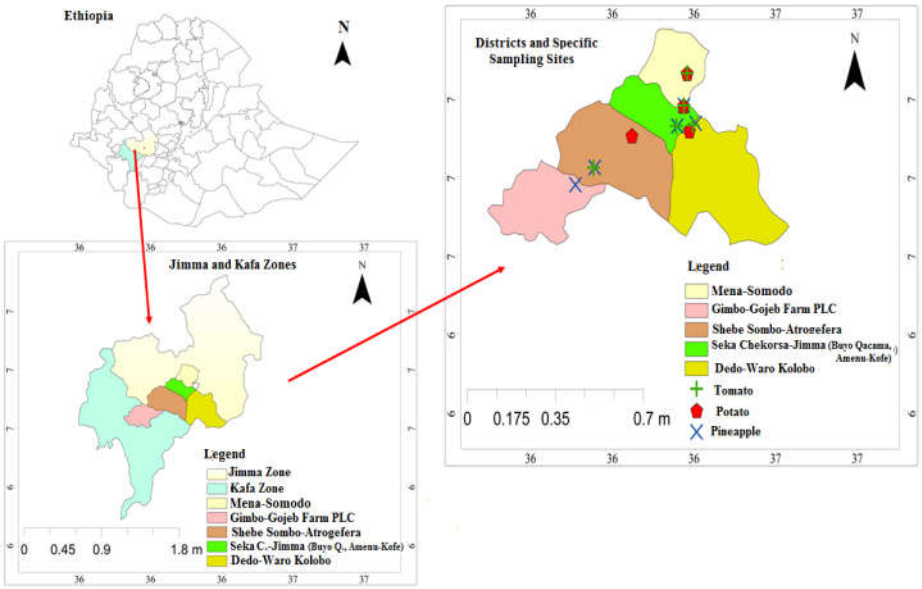

Figure 1. Map of the study area including specific sampling sites.

Instruments and equipment

Separation and quantification of the target analytes were performed using Agilent Gas chromatography equipped with an electrocapture detector (GC-ECD), autosampler, column compartment model 7980A (Agilent technologies, Singapore). An HP-5 capillary column (30 m, 0.25 mm inner diameter; 0.25-mm film thickness) coated with 5% phenyl methyl siloxane model 7890A was also obtained from Agilant technologies. A vortex mixer model FB15024 obtained from Fisher scientific (Kunstdal 21, 9900 Eeklo, Belgium) was used during sample preparation. Dispersive solid phase extraction (d-SPE) tubes packed with a mixture of primary and secondary amines (PSAs), $MgSO_4$, octadecyl (C_{18}) and graphitized carbon black (GCB) were purchased from Agilent technologies. GEEP juice blender was used for grinding and blending the samples. Elma sonicator (D-78224 Germany) was used to enhance the solubility of pesticides residues in hexane.

GC-ECD operating conditions

GC-ECD operation conditions were adopted from literature [12]. Accordingly, the GC oven temperature program was: initial set at 80 °C; ramped at 30 °C/min to 180 °C; ramped at 3 °C/min to 205 °C, held for 4 min; again ramped at 20 °C/min to 290, held for 8 min and finally ramped

at 50 °C/min to 325 °C. Nitrogen (99.99% purity) was used as a carrier gas at a flow rate of 20 mL/min and as a makeup gas at a flow rate of 60 mL/min. An aliquot of 1 µL was injected in split mode at the split ratio of 50:1 and the injection temperature was set at 280 °C. Under these conditions the total GC analysis run time was about 28 min. The pesticide residues were detected with µ-ECD, which was operated at the temperature of 300 °C.

Sample extraction and clean-up procedure

The edible portion of tomato, potato, and pineapple samples were cut into four equal segments (quartered) with stainless steel knife and then, the opposite segments were discarded. The remaining opposite segments were blended or homogenized using the pre-cleaned juice machine blender (mixer).

The standard QuEChERS procedure AOAC-2007 [14] was used for the extraction and clean-up of the target pesticides residues from the samples. Accordingly, 10 g of each homogenized tomato, potato, and pineapple sample was separately taken into a 50 mL falcon centrifuge tube. Subsequently, 10 mL acetonitrile (MeCN) containing 1% glacial acetic acid (*v/v*) was added. The mixture was manually shaken for 1 min, and a mixture of 6 g $MgSO_4$ and 1.5 g CH_3COONa was added. The content was vigorously shaken for 1 min using vortex mixer and centrifuged for 10 min at 4000 rpm. Then, 6 mL of the supernatant was transferred to a 15 mL QuEChERS kit containing 400 mg PSA, 1200 mg $MgSO_4$, 400 mg C_{18} and 45 mg GCB. The content was vigorously shaken using a vortex mixer for 1 min and centrifuged for 10 min at 4000 rpm. Then, 3 mL of the extract was transferred to round bottom flask and evaporated to dryness using rotary evaporator at 25 ºC. Finally, the residue was reconstituted with 1.5 mL n-hexane and filtered using 0.22 µm nylon syringe filter into auto-sampler vial to inject 1 µL to GC-ECD for subsequent analysis.

Method validation

The analytical performance characteristics including linear dynamic ranges (LDR), limits of detection and quantification (LOD and LOQ), precision (repeatability) and percent recovery (%R) were studied [15, 16]. Linearity was studied by constructing matrix matched calibration curves by spiking and extracting the target pesticides-free pineapple sample at six concentration levels. Each concentration level was extracted in duplicates and then, each extract was injected in duplicates. The calibration curves were constructed as the peak areas versus concentration of the target analytes. The LOD and LOQ were determined as 3 and 10 times the signal to noise ratio, respectively. Precision was investigated in terms of relative standard deviation (RSD) of replicate determinations. The %R was evaluated by spiking known concentration of each target pesticide in tomato, potato and pineapple samples.

Statistical analysis

Statistical Analyses Software SAS (Version 9.0) was used for One way ANOVA ($p < 0.05$) determination. All analyses were done in replicates, i.e. duplicates extraction and duplicates GC-ECD analysis ($n = 4$).

RESULTS AND DISCUSSION

Analtical performance characteristics of the method

The peaks of the target analytes were identified by comparing with the retention times of standard pesticides. Figure 2 shows the gas chromatogram of the target analytes under these GC-ECD operating conditions.

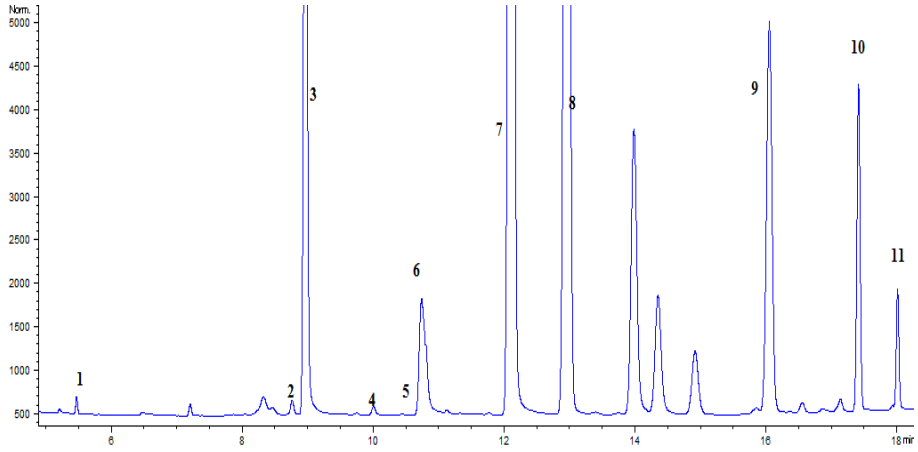

Figure 2. Chromatogram description of target analytes with their retention time (t_R), in n-hexane were: (1) Dimethoate (5.480); (2) Malathion (8.771); (3) Chloropyrifos (8.974); (4) DBC (10.015); (5) p'p-DDE (10.446); (6) Chlorf-m (10.749); (7) p'p-DDT (12.102); (8) Endrin (12.951); (9) Endosulfan sulfate (16.046); (10) Dieldrin (17.409) and (11) Methoxychlor (18.005).

The obtained calibration curves from six concentration points have exhibited wide linear ranges with satisfactory coefficient of determinations (r^2) ranging from 0.996–0.999. The LOD and LOQ of the method ranged from 0.01–1.65 and 0.03–5.51 ng/g, respectively. Table 1 shows the analytical performance characteristics of the method for analysis of the target pesticides.

Table 1. Analytical performance characteristics of the method used.

Pesticide	LDR (ng/g)	r^2	LOD (ng/g)	LOQ (ng/g)
Dimethoate	8.00 – 1600	0.998	0.90	3.00
Malathion	6.00 – 1200	0.999	1.65	5.51
Chloropyrifos	4.00 – 800	0.997	0.03	0.10
DBC	8.00 – 1600	0.999	0.91	3.04
p'p –DDE	1.00 – 200	0.996	1.21	4.03
Chlorof-m	8.00 – 1600	0.999	0.01	0.04
p'p –DDT	2.00 – 400	0.997	0.01	0.03
Endrin	2.00 – 400	0.997	0.01	0.04
Endosulfan sulfate	2.00 – 400	0.998	0.02	0.06
Dieldrin	4.00 – 800	0.999	0.12	0.39
Methoxychlor	2.00 – 400	0.997	0.09	0.30

The %R of the method were evaluated by spiking known concentrations of the standard pesticides into the samples. The obtained results of %R with their repeatability as RSD in parathesis are presented in Table 2. Except for chlorof-m in tomato and potato as well as chloropyrifos in potato samples, the obtained %R of all samples ranged from 71.22–121.56%. For all analytes, the RSD values were below 12, indicating satisfactory precision of the method. In general, the method exhibited satisfactory %R and RSD for analysis of the target pesticides residues from tomato, potato and pineapple samples [16].

-

Table 2. Percent recovery and repeatablity (n = 4) of the method.

Pesticides	Tomato	Potato	Pineapple
Dimethoate	114.83 (4.95)	73.22 (2.22)	78.78 (1.77)
Malathion	82.13 (2.78)	91.11 (6.80)	93.16 (4.15)
Chloropyrifos	82.22 (0.61)	67.90 (3.56)	98.10 (7.45)
DBC	76.38 (4.56)	85.21 (4.22)	84.72 (1.60)
p'p –DDE	96.85 (2.94)	72.19 (9.49)	73.51 (9.59)
Chloref-m	68.54 (1.75)	65.65 (5.00)	121.56 (8.35)
p'p –DDT	81.92 (2.95)	81.51 (8.42)	85.36 (10.87)
Endrin	84.95 (5.69)	99.78 (9.27)	79.82 (6.61)
Endosulfan sulfate	76.99 (6.81)	82.82 (6.21)	76.02 (1.69)
Dieldrin	107.05 (3.93)	71.22 (5.35)	96.99 (5.12)
Methoxychlor	78.04 (7.38)	90.39 (5.38)	91.88 (11.09)

Residual levels of Pesticides in tomato, potato and pineapple samples

It was observed that all the tomato, potato and pineapple samples contained chloropyrifos, DBC, p'p-DDE, Chlorof-m, endosulfan sulfate and methoxychlor pesticides residues. However, from the studied OC pesticides p,p'-DDT, endrin and dieldrin were not detected in all samples. Similarly, from OP pesticides dimethoate was detected only in MN and SQ tomato samples, whereas malathion was detected in only SQ sample. Tables 3-5 show the residual concentrations of OC and OP pesticides (mean ± SD) determined in tomato, potato, and pineapple samples.

In all studied tomato samples, high concentrations of DBC and Chlorof-m were recorded. Tomato samples collected from SQ and DD contained low concentrations of chloropyrifos residues than samples collected from other District. Residues of p'p-DDE and methoxychlor were recorded at significantly higher concentrations in tomato samples collected from DD and MN, respectively. Endosulfan sulfate was detected in all studied tomato samples, but its concentrations were relatively higher in MN, SS and DD samples. Dimethoate was detected only in SQ and MN, whereas malathion was detected only in SQ tomato samples. The obtained residual concentrations of pesticides in the studied samples were below the MRL set in EU [17] and CA [18] guidelines for tomato samples.

Table 3. Residual concentrations (mean ± SD, ng/g) of the studied OC and OP pesticides in tomato samples.

Analytes	Sampling sites					LSD	MRL	
	JA	MN	SS	SQ	DD		EU [17]	CA [18]
Dimethoate	ND	58.74 ± 3.38 ^{a}	ND	6.37 ± 2.25^{b}	ND	-	10.00	500.00
Malathion	ND	ND	ND	18.11 ± 2.75	ND	-	20.00	500.00
Chlorpyrifos	2.97 ± 0.03^{a}	2.76 ± 0.58^{ab}	2.96 ± 0.03^{a}	2.27 ± 0.02^{c}	2.49 ± 0.02^{c}	0.41	10.00	NA
DBC	2372.22±3.55^{d}	2623.74±7.61^{b}	2587.09±2.64^{c}	2647.14±3.83^{a}	2238.72±2.93^{e}	7.12	NA	NA
p,p'-DDE	1.33 ± 0.01^{b}	1.26 ± 0.21^{b}	1.31 ± 0.07^{b}	1.20±0.02^{b}	1.64 ± 0.17^{a}	0.18	50.00	NA
Chlorof-m	430.33 ± 2.98^{d}	1585.63± 6.20^{a}	423.65 ± 1.50^{d}	456.33 ± 2.90^{c}	785.57 ± 8.52^{b}	7.62	NA	NA
p,p'-DDT	ND	ND	ND	ND	ND	-	50.00	NA
Endrin	ND	ND	ND	ND	ND	-	10.00	50.00
Endosulfan sulfate	0.94 ± 0.03^{c}	1.55 ± 0.21^{a}	1.46 ± 0.07^{ab}	1.28 ± 0.02^{b}	1.53 ± 0.15^{a}	0.20	50.00	500.00
Dieldrin	ND	ND	ND	ND	ND	-	10.00	100.00
Methoxychlor	2.88 ± 0.18^{bc}	3.25 ± 0.04^{a}	3.01 ± 0.14^{b}	2.84 ± 0.08^{c}	1.71 ± 0.03^{d}	0.14	10.00	NA

MN: Mana; JA: Jimma Amenu; SS: Shebe sombo; SQ: Saka buyo qacama; DD: Dedo; LSD: Least Significant Difference; ND: Not Detected; NA: Not Available; CA: Codex Alimentarius; EU: European Union; MRL: Maximum Residue Limit; SD: Standard Deviation.

Table 4. Residual concentrations (mean ± SD, ng/g) of the studied OC and OP pesicides in potato samples.

Analytes	Sampling sites					LSD	MRLs	
	JA	MN	SS	SQ	DD		EU [17]	CA [18]
Dimethoate	ND	ND	ND	ND	ND	-	10.00	50.00
Malathion	ND	ND	ND	ND	ND	-	20.00	500.00
Chloropyrifos	2.07 ± 0.11^{ab}	2.15 ± 0.02^{a}	1.73 ± 0.03^{c}	1.91 ± 0.05^{bc}	1.89 ± 0.32^{bc}	0.22	10.00	2000.00
DBC	2859 ± 5^{b}	2881 ± 4^{a}	2262 ± 7^{d}	2329 ± 11^{c}	1866 ± 12^{e}	12.29	NA	NA
p,p'-DDE	1.36 ± 0.07^{b}	1.38 ± 0.04^{b}	1.68 ± 0.11^{a}	1.41 ± 0.22^{b}	1.13 ± 0.15^{c}	0.15	50.00	NA
Chlorof-m	799.99 ± 1.20^{b}	841.04 ± 2.05^{a}	772.89 ± 1.18^{c}	767.58 ± 6.20^{d}	633.19 ± 0.74^{e}	4.58	NA	NA
p,p'-DDT	ND	ND	ND	ND	ND	-	50.00	NA
Endrin	ND	ND	ND	ND	ND	-	10.00	50.00
Endosulfan sulfate	1.44 ± 0.03^{b}	1.43 ± 0.06^{b}	1.61 ± 0.08^{a}	1.51 ± 0.11^{ab}	1.43 ± 0.04^{b}	0.11	50.00	50.00
Dieldrin	ND	ND	ND	ND	ND	-	10.00	100.00
Methoxychlor	2.72 ± 0.24^{a}	2.29 ± 0.09^{b}	2.52 ± 0.31^{ab}	2.49 ± 0.12^{ab}	2.68 ± 0.24^{a}	0.37	10.00	NA

Table 5. Residual concentrations (mean ± SD, ng/g) of the studied OC and OP pesicides in pineapple samples.

Analytes	Sampling sites					LSD	MRLs	
	JARC	GH	SS	SQ	DD		EU [17]	CA [18]
Dimethoate	ND	ND	ND	ND	ND	-	10.00	5000.00
Malathion	ND	ND	ND	ND	ND	-	20.00	7000.00
Chloropyrifos	2.95 ± 0.05^{a}	2.12 ± 0.10^{e}	2.26 ± 0.03^{d}	2.61 ± 0.02^{c}	2.78 ± 0.03^{b}	0.07	10.00	1000.00
DBC	2672.53 ± 6.23^{b}	2749.67 ± 3.80^{a}	2504.62 ± 7.35^{d}	2580.88 ± 9.53^{c}	1542.46 ± 9.53^{e}	10.28	NA	NA
p,p'-DDE	1.89 ± 0.01^{a}	1.93 ± 0.01^{a}	1.41 ± 0.02^{d}	1.77 ± 0.02^{b}	1.56 ± 0.06^{c}	0.05	50.00	NA
Chlorof-m	664.19 ± 6.63^{c}	1355.57 ± 6.20^{a}	738.15 ± 2.63^{b}	614.18 ± 7.05^{d}	367.88 ± 7.05^{e}	10.02	NA	NA
p,p'-DDT	ND	ND	ND	ND	ND	-	50.00	NA
Endrin	ND	ND	ND	ND	ND	-	10.00	50.00
Endosulfan sulfate	1.47 ± 0.01^{d}	1.27 ± 0.01^{e}	2.21 ± 0.01^{a}	1.90 ± 0.13^{b}	1.75 ± 0.14^{c}	0.13	50.00	5000.00
Dieldrin	ND	ND	ND	ND	ND	-	10.00	50.00
Methoxychlor	8.78 ± 0.30^{a}	8.72 ± 0.73^{a}	2.83 ± 0.18^{d}	7.75 ± 0.05^{b}	5.50 ± 0.01^{c}	0.50	10.00	NA

JARC = Jimma agricultural research center; GH = Gojeb Horizion plantation PLC.

Similar to tomato sample, the p'p-DDE contamination status of SS potato sample was significantly higher than potato samples collected from other sites. Statistical analysis showed that there were significant differences among the concentrations of chloropyrifos in potato samples collected from different sites. The concentrations of endosulfan sulfate and methoxychlor in the studied samples were varied from 1.43–1.61 and 2.29–2.72 ng/g, respectively. Like the tomato samples, potato samples also contained very high concentrations of DBC and chlorofl-methyl. As in the case of tomato and potato samples, pineapple samples also contained the highest residual concentrations of DBC, followed by Chlorof-m. The concentrations of chloropyrifos in pineapple samples ranged from 2.12 - 2.95 ng/g; with minimum and maximum concentrations in GH and JARC, respectively. The pineapple samples contained DBC from 2504.62 - 2749.67 ng/g; Chlorof-m 367.88–1355.57 ng/g; metabolite of DDT insecticide, DDE 1.41–1.93 ng/g; endosulfan sulfate 1.27–2.21 ng/g; and methoxychlor 2.82–8.78 ng/g. The statistical test showed that there were significant differences (at $p < 0.05$) in the residual concentrations of the detected pesticides among the pineapple samples collected from different sampling sites.

From the studied OC pesticides chlorof-m was found at very high concetrations in all tomato, potato and pineapple samples. Its lowest (367.88 ng/g) and highest (1585.6 ng/g) concentrations were recorded in DD and MN pineapple and tomato samples, respectively. Next to chlorof-m, higher concentrations of dimethoate and malathion were detected in MN and SQ tomato samples. The detected residual concentrations of chloropyrifos were almost similar in all the studied samples. These results confirmed that chloropyrifos is used in the study area for the control of

different pests from tomato, tomato and pineapple farmlands. Chlorpyrifos is broad-spectrum systemic insecticidal activities. it is widely used to control various agricultural pests such as cutworms, corn rootworms, cockroaches, grubs, flea beetles, flies, termites, fire ants, and lice [19].

In all samples, p'p -DDT was not detected, this may indicate that DDT was not recently used in the area. Because it has officially banned for agricultural applications in Ethiopia. However, its methabolite p'p-DDE was detected in all tomato, potato and pineapple samples indicating that the parent pesticide, p'p -DDT, was used in the area. Until recent years, DDT was also used in Ethiopia for the prevention of malaria and aslo illegally used by some people from obsolete pesticide stocks [12].

The detected residual concentrations of DBC and chlorof–m were significantly different among the sampling sites of tomato, potato, and pineapple samples. The minimum residual concentration of DBC, 1542.46 ng/g, was detected in DD pineapple sample and its maximum concentration, 2881.13 ng/g, was detected in MN potato sample. Similarly, th minimum concentration of chlorof–m (367.88 ng/g) was aslo detected in DD pineapple sample whereas its maximum concentration, 1585.63 ng/g, was detected in MN tomato sample. The detected residual concentrations of DBC and chlorof–m were far above the EU general default MRL, i.e., 10 ng/g. However, none of the interviewed farmers confirmed that these pesticides have recently been used in the area. Therefore, the presence of these pesticides in the studied samples might be related to its historical use and environmental contamination, owing to its environmental persistence and huge accumulation of the obsolete OC pesticides in the country [20, 21]. Furthermore, in all the studied samples more than one pesticides were detected, indicating that tomato, potato, and pineapple cultivated in the study area are highly susceptible to pests and thus, require applications of different pesticides [22].

Compared with other studies reported from other countries such as Iran [22], Bangladesh [23], Ghana [24], Egypt [25], and Bolivia [26] the studied tomato, potato and pineapple samples contained lower concentrations of OC and OP pesticide residues, except MN tomato sample which contained very high concentration of dimethoate than the reported values (Table 6). However, MN tomato sample contained higher concentrations of dimethoate than the reported values in tomato collected from Ghana [24]. The detected concentrations of chloropyrifos in all three samples were far below its residual concentrations reported in tomato samples from Iran [22], Ghana [24], and Bangladish [23] ; in potato samples from Egypt [25]and Bolivia [26] and pineapple samples from Ghana [24]. Earlier report study also showed that tomato and onion samples collected from Piaza Atikilt Tera, Addis Ababa, Ethiopia contained residues of OC pesticides [3].

Table 6. Residue levels of pesticides in other countries compared with Ethiopia.

Country	Pesticides	Conc. (ng/g)	Food items	References
Ethiopia	DDT	1.0	Tomato	[3]
	Endosulfan sulfate	0.5		
Bangladesh	Chlorpyrifos	342.00*	Tomato	[23]
Iran	Chlorpyrifos	13 - 51	Tomato	[22]
	Malathion	NA		
	Methoxychlor			
	DDT			
	p'p –DDE			
	Aldrin			
Ghana	Methoxychlor	4.00	Tomato	[24]
	Dieldrin	4.00		
	Endrin	ND		
	p'p –DDE	13.00		

	p'p –DDT	12.00		
	Dimethoate	13.00*		
	Chloropyrifos	26.00*		
	Malathion	38.00*		
Egypt	Chlorpyrifos	9.00 - 40.00*	Potato	[25]
	p'p – DDE	9.00		
Bolivia	Chlorpyrifos	730.00*	Potato	[26]
Ghana	Malathion	6.00	Pineapple	[24]
	Methoxychlor	31.00*		
	Dieldrin	12.00*		
	Endrin	4.00		
	p'p –DDE, p'p –DDT	ND		
	Dimethoate	6.00		
	Chloropyrifos	55.00*		
Ethiopia	Dimethoate	6.37 - 58.74*	Tomato, Potato and Pineapple	Present study
	Malathion	18.11*		
	Chloropyrifos	1.73 - 2.97		
	p'p –DDE	1.13 - 1.93		
	p'p –DDT, Endrin, & Dieldrin	ND		
	Endosulfan sulfate	0.94 - 2.21		
	Methoxychlor	1.71 - 8.78		

*indicates values > EU MRLs.

CONCLUSION

In this study, the residual concentrations of some selected OP and OC pesticides were determined in tomato, potato, and pineapple samples collected from selected farmlands from Jimma zone (Oromia reginal state) and Kefa zone (South West Ethiopian peoples at regional state). The three agricultural products contained one or more residues of the studied pecticides. Among these pesticides, the residual concentrations of DBC and chlorof-m in all the studeid samples were far above EU general default MRL. Pesticides such as p'p-DDT, endrin, and dieldrin were not detected in all samples. Dimethoate was detected only in SQ and MN tomato samples. Similarly, malathion was detected only in SQ tomato sample. Pesticides including chloropyrifos, endosulfan sulfate, DDE and methoxychlor were recorded in all the studied tomato, potato and pineapple samples, but their detected concentrations were below their MRL set in EU and CA guidelines. One way ANOVA results at $p \leq 0.05$ revealed the presence of significant differences in the residual concentrations of the detected pesticides among the sampling sites of the tomato, potato and pinapple samples. In general, the study results indicated that regular monitoring of pesticides residues in agricultural products of the arera is mandatory.

ACKNOWLEDGMENTS

We acknowlege Ethiopian Institute of Agricultural Research (EIAR) and Jimma University for financeal support.

REFERENCES

1. Daba, D.; Hymete, A.; Bekhit, A.A.; Mohamed, A.M.; Bekhit, A.E. Multi-residue analysis of pesticides in wheat and khat collected from different regions of Ethiopia. *Bull. Environ. Contam. Toxicol.* **2011**, 86, 336-341.
2. Mengistie, B.T. Environmental governance of pesticides in Ethiopian vegetable and cut flower

production. PhD thesis, Wageningen University, Wageningen, The Netherlands, **2016**.
3. Geletu, A. Organochlorine pesticide residues in orange and tomato samples from Piasa Atekelt Tera, Addis Ababa. MSc Thesis, Addis Ababa University, Addis Ababa, Ethiopia, **2009**.
4. Fernández-Alba, A.R.; García-Reyes, J.F. Large-scale multi-residue methods for pesticides and their degradation products in food by advanced LC-MS. *Trends Anal. Chem.* **2008**, 27, 973-990.
5. Hassaan, M.A.; El Nemr, A. Pesticides pollution: Classifications, human health impact, extraction and treatment techniques. *Egypt. J. Aquat. Res.* **2020**, 46, 207-220.
6. Fenik, J.; Tankiewicz, M.; Biziuk, M. Properties and determination of pesticides in fruits and vegetables. *Trends Anal. Chem.* **2015**, 30, 814-826.
7. Bempah, K.C.; Buah-kwo, A.; Enimil, E.; Blewu, B.; Agyei-Martey, G. Residues of organochlorine pesticides in vegetables marketed in Greater Accra Region of Ghana. *Food Control* **2012**, 25, 537-542.
8. Fikadu, Z. Pesticides use, practice and its effect on honeybee in Ethiopia: a review. *Food Sci. Qual. Manag.* **2019**, 92, 11-21.
9. Mengistie, B.T. Policy-practice nexus: Pesticide registration, distribution and use in Ethiopia. *SM J. Environ. Toxicol.* **2016**, 2, 1006.
10. Loha, K.M.; Lamoree, M.; Weiss, J.M.; de Boer, J. Import, disposal, and health impacts of pesticides in the East Africa Rift (EAR) Zone: a review on management and policy analysis. *Crop Prot.* **2018**, 112, 322-331.
11. Malhat, F.M.; Loutfy, N.M.; Greish, S.S.; Ahmed, M.T. A Review of environmental contamination by organochlorine and organophosphorus pesticides in Egypt. *J. Toxicol. Risk Assess.* **2018**, 4, 1-17.
12. Mekonen, S.; Ambelu, A.; Spanoghe, S. Pesticide residue evaluation in major staple food items of ethiopia using the QuEChERS method : a case study from the Jimma Zone. *Environ. Toxicol. Chem.* **2014**, 33, 1294-1302.
13. Mekonen, S.; Ambelu, A.; Negassa, B.; Spanoghe, P. Exposure to DDT and its metabolites from khat (*Catha edulis*) chewing : Consumers risk assessment from southwestern Ethiopia. *Regul. Toxicol. Pharmacol.* **2017**, 87, 64-70.
14. Lehotay, S.J.; Valverde, A. Determination of pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulfate: collaborative study. *J. AOAC Int.* **2007**, 90, 485-520.
15. Lavanya, G.; Sunil, M.; Eswarudu, M.M.; Chinna Eswaraiah, M.; Harisudha, K.; Naga Spandana, B. Analytical method validation: an updated review. *Int. J. Pharm. Sci. Res.* **2013**, 4, 1280-1286.
16. Ngan, C.K.; Khairatul, A.M.; Shahid, S.M.; Ismail, B.S. Validation of a ' multi-residue ' analytical method for pesticide residue analysis in fruits. *J. Trop. Agric. and Fd. Sc.* **2013**, 41, 119-126.
17. EU pesticides database. Available at: https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/mrls/?event=search.pr. Accessed on August, **202**2
18. Codex Alimentarius; Pestide database: available at: https://www.fao.org/fao-who-codexalimentarius/codex%20texts/dbs/pestres/pesticides/en, Accessed, August **2022.**
19. Hill, M.P.; Macfadyen, S.; Nash, M.A. Broad spectrum pesticide application alters natural enemy communities and may facilitate secondary pest outbreaks. *Peer J.* **2017**, doi.org/10.7717/peerj.4179.
20. Botero-Coy, A.M.; Marín, J.M.; Serrano, R.; Sancho, J.V.; Hernández, F. Exploring matrix effects in liquid chromatography-tandem mass spectrometry determination of pesticide residues in tropical fruits. *Anal. Bioanal. Chem.* **2015**, 407,3667-3681.
21. Wittayanan, W.; Chaimongkol, T.; Jongmevasna, W. Multiresidue method for determination

of 20 organochlorine pesticide residues in fruits and vegetables using modified QuEChERS and GC-ECD/GC-MSD. *IFRJ* **2017**, 24, 2340-2346.
22. Salamzadeh, J.; Shakoori, A.; Moradi, V. Occurrence of multiclass pesticide residues in tomato samples collected from different markets of Iran. *J. Environ. Health Sci. Eng.* **2018**, 16, 55-63.
23. Fardous, Z.; Islam, M.N.; Hoque, S.M.; Chowdhury, M.A.Z.; Rahman, M.A. Determination of some selected pesticide residues in tomato from different locations of Bangladesh. *Int J Sustain Agric Tech.* **2007**, 3, 4-7.
24. Okoffo, E.D.; Fosu-Mensah, B.Y.; Gordon, C. Contamination levels of organophosphorus and synthetic pyrethroid pesticides in cocoa beans from Ghana. *Food Control* **2017**, 73, 1371-1378.
25. Ahmed, M.A.I.; Khalil, N.S.; Rahman, T.A.A.E. Determination of pesticide residues in potato tuber samples using QuEChERS method with gas chromatography. *Aust. J. Basic Appl. Sci.* **2014,** 8, 349-353.
26. Skovgaard, M.; Encinas, S.R.; Chresten, O.; Andersen, J.H.; Condarco, G.; Jørs, E. Pesticide residues in commercial lettuce, onion, and potato samples from pesticide residues in commercial lettuce, onion, and potato samples from Bolivia - a threat to public health?, *Environ. Health Insights* **2017**, 11, 1-8.