Research article

Residue analysis of selected organophosphorus and organochlorine pesticides in commercial tomato fruits by gas chromatography mass spectrometry

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A B S T R A C T

In this study, analysis of some selected organophosphorus and organochlorine pesticides was carried out in tomato samples collected from the markets of Mettu town, Ilu Aba Bora Zone, Oromia, Ethiopia. The quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) method was used for the extraction of collected samples using acetonitrile with 1% acetic acid, anhydrous magnesium sulfate, and anhydrous sodium acetate, followed by dispersive solid-phase extraction (d-SPE). Chromatographic separation and quantitative determination of the pesticides were performed by gas chromatography equipped with a mass spectrometer. The calibration curves for each analyte constructed in tomato samples were linear in the concentration range of 2–200 μg/kg with $R^2 > 0.99$ and the LODs and LOQs of the method were in the range of 0.01–0.04 μg/kg and 0.04–0.13 μg/kg, respectively. The recovery and precision study results were within acceptable standard guidelines. Of the fourteen pesticides tested, chlordane, hexachlorobenzene, 4, 4'-DDE, 4, 4'-DDD, 4, 4'- DDT, and profenofos were detected at 0.15, 0.09, 0.17, 0.032, 1.24 and 0.062 μg/kg, respectively. Despite the concentrations of the detected pesticides being lower than the maximum residue limit recommended by FAO/WHO, the presence of these toxic chemicals in tomatoes indicates product contamination and requires extensive further investigation with the inclusion of other pesticides.

1. Introduction

Pesticides are both synthetic and naturally occurring biological substances that slay and rheostat pests, such as insects, rodents, plants, and fungi that damage our food, health, or environment; insecticides, fungicides, and handlings to protect food in storage. These chemicals are applied during farming, transportation, and storage [1,2]. Agricultural production has been considerably improved with the help of pesticides but their unrestricted and extreme use is polluting the atmosphere, foodstuffs, and aquatic and agricultural products [3]. Certain manmade substances are exceptionally herbicides, and molluscicides are some of the classes besides plant growth regulators, wood preservatives resilient to biodegradation by intrinsic flora than naturally occurring organic compounds that are easily degraded upon introduction into the environment [4]. Pesticides are accepted as a lucrative way of controlling pests and improving yield and food quality. Despite their valuable effect on agricultural productivity, unselective use causes various somber complications to the environment and human health, since they are noxious to non-target species [5].

The most widely used pesticides in developing countries are primarily organochlorines, organophosphorus, synthetic pyrethroids, and carbamates [6]. Insecticides consist of a varied class of compounds but the most protuberant for plant treatment are chlorine and phosphorus having compounds. Organophosphorus pesticides (OPPs) are slowly replacing organochlorines due to their high bio-accumulation effect [7,8]. OPPs are derivatives of phosphoric or phosphonic acid in form of amides, esters, or thiols. They do not persist in the environment for longer periods as they are easily hydrolyzed [9,10]. Nevertheless, their numerous poisonousness (they act as inhibitors of acetylcholinesterase enzyme), as well as the likelihood of build-up in the food chain, can cause a menace to human health [11–13].

Organophosphate pesticides interfere with growth-stimulating mechanisms by hindering various enzymes, transcuticular diffusion, and penetrability which is vital for the growth of plants. They can also deter the activities of the enzyme in aquatic and terrestrial organisms leading to, hepatic reproductive, respiratory, nervous, and renal anomalies. Regular uses of organophosphate pesticides decrease the microbial community that affects soil fertility [9,14] Chlorpyrifos, dimethoate, profenofos, and others are eminent organophosphate pesticides used for different purposes in agriculture, horticulture in pest controlling [9,15,16].

Organochlorine pesticides (OCPs) are multipurpose chlorinated hydrocarbon substances. Most of them are categorized as persistent organic pollutants (POPs), a class of chemicals known to degrade very slowly and bio-accumulates in lipid-rich tissue such as body fat [17]. They are mainly used as insecticides that include DDT, lindane, endosulfan, aldrin, dieldrin, and chlordane [18]. Due to their ubiquitous nature, lipophilic properties, and persistence in the environment, pesticides tend to accumulate in the tissues of living organisms [19]. They disrupt endocrine system of animals and humans as they augment the efficiency of thyroid hormones [20]. Many countries have set rules and regulations in monitoring pesticide residues in food commodities to confirm whether the levels adhere to the national or international guidelines [21–23].

The QuEChERS technique is a very feasible method and irrespective of the use of high organic solvents and time consuming, it can extract varied classes of pesticide remains in numerous agricultural and horticultural matrices [24,25]. It requires minimum reagent consumables and a short pretreatment period, so it is accepted by many experimenters and international associations like AOAC and European standardization committee [26]. The major steps in both methods includes acetonitrile extraction, dispersive solid phase clean up using primary secondary amine and magnesium sulfate. The purposes of further method modification are decreasing time of sample preparation and analysis, minimize extraction solvents and glasswares used and upsurge the sensitivity of the method.

Ethiopia had also been considered the largest destination for obsolete pesticides in the horn of Africa. The Ethiopian Ministry of Agriculture and Livestock Resources, Plant and Animal Health Directorate registered 409 pesticides by 53 registrants in 2016 for different purposes, of which the majorities were insecticides [27]. This includes chlordane, DDT, dieldrin, and lindane which are banned or restricted in most countries [28]. 57.7% of the registered pesticides were listed under the 2018 PAN HHPs (highly hazardous pesticide) list. The information from the African Stockpiles Project shows that there are more than 350 metric tonnes of obsolete stockpiles of POPs present in Ethiopia including the studied organochlorine pesticides [29]. Even though pesticides are widely used in Ethiopia; their frequent monitoring of fruits and vegetables is almost absent. Thus, pesticide residue is a threat to the export of fruits and vegetables from Ethiopia besides its impact on human health [30–33]. Hence, this study was conducted on tomato fruit samples sold in Mettu town, Ilu Aba Bora Zone, Oromia, Ethiopia, to assess the residue level of selected organophosphorus and organochlorine pesticides using QuEChERS for sample extraction with d-SPE clean-up followed by the GC-MS detection system.

2. Materials and methods

2.1. Chemicals and reagents

Reagent-grade or pesticide-grade (α-Lindane, Hexachlorobenzene, Dimethoate, Heptachlor, aldrin, heptachlor epoxide, chlordane, endosulfan I, profenofos, 4,4'-DDE (Dichloro-diphenyldichloroethylene), endosulfan II, 4,4'-DDD (Dichlorodiphenyldichloroethane), 4,4'-DDT (Dichlorodiphenyltrichloroethane) and Methoxychlor) chemicals used in all tests were obtained from Sigma-Aldrich (Germany). Standard solutions (stock, composite, calibration, and surrogate (analyte) were stored at < 6 °C in polytetrafluoroethylene (PTFE)-sealed containers in the dark. Anhydrous magnesium sulfate (MgSO₄), n-hexane, acetonitrile (CH₃CN), ethyl acetate (C₄H₈O₂), glacial acetic acid (CH₃COOH), Bondesil-primary secondary amine (PSA, 40 μm) and sodium acetate (NaCH₃COO) were supplied from Sigma-Aldrich (Germany).

2.2. Sample extraction (QuEChERS)

Fifty tomato samples were collected between September 2020–June 2021 from fifteen different places (3 from the shop and 12 from the open markets) and stratified into 3 based on their size: small, medium, and large. From each stratum portions (60–100 g) were taken to form a 2 kg composite sample. Different masses (5–15 g) of this composite tomato sample were used in the analysis of pesticides.

The tomato sample extraction and partitioning were carried out according to a modified version of the QuEChERS procedure with the d-SPE clean-up method as per the official method of AOAC 2007.1 [34] as follows: 15 g aliquot of the chopped and homogenized sample of tomatoes fruit was weighed into 50 mL plastic centrifuge tubes on a sensitive analytical balance and left to hydrate for 30 min after the addition of 10 mL distilled water and stirring for 30 s. Two Ceramic homogenizers (part number 5982–9313) were added to each 50 mL tube. Then, 10 mL of acetonitrile with 1% glacial acetic acid (v/v) (buffering media) was added into the homogenized tomato sample using a micropipette, and samples were shaken by hand for 1 min to upsurge interaction between the solvent and the sample for each pesticide analytes. 6 g Magnesium sulfate and 1.5 g sodium acetate were then added (Agilent QuEChERS part number

59825755) followed by vigorously shaking the sealed tubes for 1 min by vortex mixer and centrifuging for 5 min at 4500 rpm.

2.3. Dispersive SPE clean-up

A 6-mL aliquot amount of the (upper) acetonitrile layer was transferred into Agilent Bond Elut QuEChERS EN d-SPE 15-mL plastic centrifuge tubes (Part number 5982-5456) containing primary secondary amine (150 mg) PSA. Next, 5 mL of 20% (w/w) aqueous sodium chloride solution and 1 mL n-hexane were added. The tube was robustly vortexed for 1 min and then centrifuged for 2 min at 4500 rpm. A portion of the (upper) n-hexane layer was filtered through a Teflon filter 0.45 μm and 1–2 mL of extracted were transferred into an autosampler vial for injection into the GC-MS system.

2.4. Calibration standards

10 μg of each pesticide were dissolved in 10 mL volumetric flasks containing acetonitrile to prepare 1 mg/L or 1000 ppb of each pesticide stock standard solutions and stored in a refrigerator below 6 °C. Calibration standard solutions of the fourteen pesticides with concentration ranges of 2–200 ppb (w/w) spiked with sample matrix were prepared in acetonitrile and stored at 4 °C. Other working solutions were prepared by dilutions of intermediate solutions.

2.5. Method validation

According to the European SANCO guidelines [35], the validation study was tested to assess for linearity, recovery, precision, limits of detection (LOD), and quantitation (LOQ). The linearity of the method was studied with calibrations of standard pesticide solutions at six concentration levels (2, 5, 20, 50, 100, and 200 μg/kg) for each analyte. At all concentration levels, the recoveries (to estimate the accuracy of the method) were determined by spiking different concentrations of pesticide standards with tomato samples. Solutions at each spiked level were prepared in triplicate and were injected. Spiked samples were left to stand for at least 1 h to allow pesticide absorption into the sample. They were then extracted according to the extraction procedures described above.

2.6. Analytical instrumentation and conditions

Analysis was made by the Agilent 5977B GC/MSD Gas chromatograph (Agilent Technologies, USA) coupled with a mass spectrometer (5977B MS). The sample was introduced in splitless mode. A DB-5 MS column with 30 m × 0.25 mm x 0.25 μm was used. A fused silica capillary column, 5%-phenyl-methylpolysiloxane as stationary phase (30 m × 0.25 mm i.d.) and 0.25 μm film thickness (Quadrex, Woodbridge, U.S.A) was used with helium as carrier gas at a constant flow (1 mL/min). The system was equipped with a split-splitless injection inlet and a 1 μL aliquot of sample or standard was injected in splitless mode at 250 °C. The GC oven was operated with the following temperature program: initial temperature 100 °C held for 3 min, ramped at 25 °C/min to 175 °C not held, followed by a ramp of 8 °C/min to 290 °C and held for 5 min. The total run time was 25 min and XCalibur1.2 chromatography data system software was used for instrument control and data analysis. The transfer line temperature was set at 275 °C and the source temperature at 175 °C. MS experimental conditions: Ionization mode: EI, EMV mode: Gain Factor, Gain Factor: 1, Transfer line temperature: 275 °C, Ion Source temp: 230 °C, Quad temp: 150 °C, Solvent delay: 3 min. The mass spectrometer was operated in selected ion monitoring mode (SIM) [36].

Table 1
Identification/quantitation and linearity parameters used for pesticides residue analysis.

Analyte	Retention Time (RT) in minutes ($\overline{X}$ ± SD)	Time segment (min)	Quantifier ion (m/z)	Qualifier ions (m/z)	Regression line	R^2
Dimethoate	10.711 ± 0.03	10.623-10.778	93	87, 125	Y = 2.73X+60.83	0.999
Profenofos	23.233 ± 0.03	23.201-23.222	339	337, 374	Y = 3.85X −4.26	0.999
Chlordane	20.748 ± 0.01	20.677-20.948	373	375, 377	Y = 9.18X +17.24	0.999
Endosulfan I	21.533 ± 0.02	21.470-21.637	195	170, 237	Y = 8.11 + 1.35	0.999
Endosulfan II	24.560 ± 0.01	25.572-25.572	237	339, 341	Y = 5.35X-22.56	0.999
α-Lindane	10.182 ± 0.01	10.159-10.360	181	219, 109	Y = 39.29X +28.83	0.999
Hexachlorobenzene	10.306 ± 0.01	10.205-10.484	284	142, 249	Y = 125.81X +165.99	0.999
Heptachlor	14.910 ± 0.01	14.852-15.024	272	100, 237	Y = 31.15X +22.26	0.999
Aldrin	16.810 ± 0.01	16.797-16.959	263	293, 101	Y = 39.54X +101.70	0.999
Heptachlor epoxide	19.206 ± 0.01	19.150-19.328	353	263, 81	Y = 42.86X +80.04	0.999
4,4'-DDE	23.397 ± 0.01	23.316-23.567	246	318, 176	Y = 169.08X +221.75	0.999
4,4'-DDD	26.115 ± 0.01	26.035-26.271	235	165, 237	Y = 170.21X +291.14	0.999
4,4'-DDT	27.713 ± 0.01	27.667-27.774	235	237, 165	Y = 96.36X + 73.96	0.999
Methoxychlor	29.670 ± 0.01	29.655-29.733	227	152, 212	Y = 164.71X - 260.61	0.999

3. Result and discussion

3.1. Chromatographic analysis

The analytical parameters for fourteen different chemical pesticides were developed with the analytical conditions for the GC-MS technique and QuEChERS sample extraction with d-SPE clean-up methods. The target analytes were separated with a good resolution as shown in Fig. 3.1. GC-MS analysis was used for the identification and quantification of pesticides in tomato fruits. Concentration and identity determinations of the analytes were done based on the use of one transition ion, at least one qualifier ion, and retention times. Table 1 summarizes retention time, quantifier ion, qualifier ions, and linearity parameters obtained for the studied pesticides. A chromatogram of 50 ppb of each pesticide standard solution is shown in Fig. 1.

The mass spectra (full scan) of fourteen pesticides were used to choose the greatest abundant mass-to-charge (m/z) ions. The choice of a minimum of three different ions (for validation and quantification) for all the analytes met the requirements as per the SANTE/ 12682/2019 guideline [35]. Retention time (RT) was used for identification and separation with good resolution of the peaks as follows in Table 3.1 the MS setting of SIM scan time segments for each analyte was at 2 μg/kg while the average retention times and calibration lines were determined taking the concentration ranges of 2–200 μg/kg.

Where $\overline{X}$ is the mean and SD is the standard deviation (n = 6)

After running GC-MS, peaks were identified by their retention time and mass spectra. An ion with the highest percentage abundance and exhibited no indication of chromatographic meddling was taken for concentration determination. The retention time range is 10.182 ± 0.009–29.670 ± 0.008, the minimum RT corresponding to α-Lindane, and the maximum was for Methoxychlor.

3.2. Validation of the method

3.2.1. Linearity

Linearity was studied by constructing analytical curves by running GC-MS of a standard solution containing respective analytes by the dilution of the standard stock solution. The standard curves for each pesticide acquired good linearity in the range of 2–200 μg/kg with the correlation coefficient (R^2) > 0.99, the regression line (y = bx + a), where y is the detector response (signal), b is the slope and a is the y-intercept and R^2 is correlation coefficient, as shown in Table 2.

The plots of calibration curves at 2–200 μg/kg (Figs. 1S–14S) and GC-MS spectra at 50 μg/kg (Figs. 15S–28S) of the fourteen pesticide standards in Table 1 are shown under supporting materials.

3.2.2. Recovery and precision

To validate the accuracy of the method, a recovery study was done by spiking pesticide standards at different concentrations (20, 50, and 100 μg/kg) with 15 g of homogenized tomato samples whose results are shown in Table 2.

Where $\overline{X}$ the mean and % RSD is the percent relative standard deviation

The method validated for residue analysis of tomato fruit was suitable for the intended purpose. The accuracy and precision of the method were evaluated by spiking the tomato at six concentrations in the range of 2–200 μg/kg. The mean recoveries of tomato fruits were 71.9–108.54% (Table 2). The intraday repeatability of the method was determined by calculating the percent relative standard deviation (%RSD) of the spiked sample at three concentrations with triplicate each (n = 3). The values ranged from 8.03 to 18.39%. The range of mean recoveries at the relevant concentration level (0.01 < x ≤ 0.1 mg/kg) should be 70–120% and the precision ≤20% RSD [37].

3.2.3. Limit of detection (LOD) and limit of quantitation (LOQ)

The LODs and LOQs of the developed method for each analyte were calculated from the calibration curves indicated under the
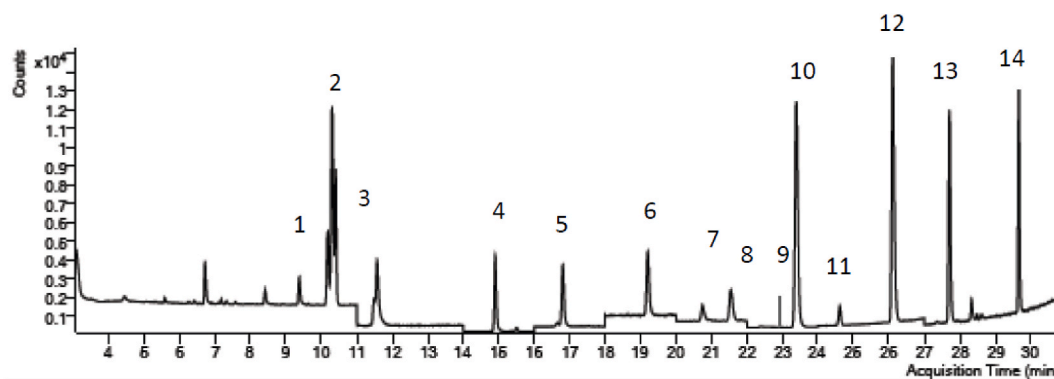

Fig. 1. Chromatogram of 50 ppb α-Lindane (1), Hexachlorobenzene (2), Dimethoate (3), Heptachlor (4), aldrin (5), Heptachlor epoxide (6), Chlordane (7), Endosulfan I (8), Profenofos (9), 4,4'-DDE (10), Endosulfan II (11), 4,4'-DDD (12), 4,4'-DDT (13) and Methoxychlor (14).

Table 2
Percentage recovery and RSD of pesticides.

Analyte	Spiked concentration (μg/kg)	Average Recovered concentration (μg/kg) (n = 3)	Mean Recovery	RSD (%)
Dimethoate	20	18.61	93.05	11.84
	50	52.37	104.74	9.21
	100	97.65	97.65	13.97
Profenofos	20	19.66	98.30	15.71
	50	48.09	96.18	12.57
	100	101.3	101.3	9.54
Chlordane	20	16.6	83.00	17.48
	50	52.51	105.02	12.63
	100	100.9	100.90	8.87
Endosulfan I	20	19.84	99.20	15.34
	50	48.58	97.16	11.94
	100	100.25	100.25	10.42
Endosulfan II	20	18.57	91.35	18.39
	50	46.01	92.02	16.23
	100	97.66	97.66	13.56
α-Lindane	20	21.20	106.00	10.48
	50	54.27	108.54	14.51
	100	104.86	104.86	8.45
Hexachlorobenzene	20	15.71	78.55	16.91
	50	49.89	99.78	12.35
	100	95.37	95.37	13.38
Heptachlor	20	14.38	71.90	16.42
	50	48.60	97.20	11.58
	100	99.24	99.24	8.92
Aldrin	20	21.46	107.30	10.54
	50	45.45	90.90	15.84
	100	99.75	99.75	8.93
Heptachlor epoxide	20	17.79	88.95	13.72
	50	49.55	99.10	9.17
	100	105.63	105.63	14.28
4,4'-DDE	20	16.31	81.55	11.47
	50	46.21	92.42	16.01
	100	100.14	100.14	8.03
4,4'-DDD	20	22.49	112.45	15.79
	50	48.91	97.82	12.04
	100	103.49	103.49	14.56
4,4'-DDT	20	17.01	85.05	10.20
	50	48.87	97.74	9.99
	100	96.28	96.28	13.07
Methoxychlor	20	19.45	97.25	8.41
	50	46.58	93.16	9.52
	100	99.94	99.94	10.58

support material. Table 3 shows the result of calculated LODs and LOQs of the studied pesticides. As it can be seen in the table the LODs of all analytes are less than the minimum concentration of pesticide used for the regression line (2–200 μg/kg) and hence are in an acceptable range. LOQs are also in good relation (LOQ ~ 3.3 LOD) with observed LODs (see Table 4). Equations (1)–(3) were used for calculating the parameters [38,39].

Table 3
LODs and LOQs of studied pesticides analytes (rounded to 2 digits).

Analyte	LOD (μg/kg)	LOQ (μg/kg)
Dimethoate	0.04	0.12
Profenofos	0.01	0.04
Chlordane	0.03	0.08
Endosulfan I	0.04	0.13
Endosulfan II	0.03	0.08
α-Lindane	0.02	0.05
Hexachlorobenzene	0.02	0.06
Heptachlor	0.02	0.05
Aldrin	0.03	0.09
Heptachlor epoxide	0.01	0.04
4,4'-DDE	0.03	0.08
4,4'-DDD	0.03	0.09
4,4'-DDT	0.02	0.07
Methoxychlor	0.04	0.12

Table 4
Comparison of studied pesticides levels and method sensitivity (LoD) with literature values.

Analyte	Concentration (µg/kg)	LoD (µg/kg)	Reference
Dimethoate	ND	0.008/	[58]
	ND–58.74	0.90/	[51]
Profenofos	322.9	0.01	[58]
Chlordane	2.09 ± 0.27	0.019	[53]
	1.02	0.070	[54]
Endosulfan I	1.3–1600	0.006µg/kg	[52]
	NR	0.025	[53]
	0.168–1183	NR	[59]
	6.64 ± 2.89	NR	[53]
Endosulfan II	0.5–690	0.012	[52]
	5	NR	[59]
	NR	0.022	[53]
α-Lindane	1660–2700	NR	[59]
	1.97 ± 0.31	0.028	[53]
Hexachlorobenzene	5.40	0.080	[54]
Heptachlor	ND	NR	[59]
	NR	0.024	[53]
	0.33	0.11	[54]
Aldrin	ND	NR	[59]
	1.57 ± 0.87	0.023	[53]
4,4'-DDE	300–3200	0.029	[52]
	1.20-1.64	1.21	[51]
	ND	NR	[59]
	1.43 ± 0.15	0.019	[53]
	0.44	0.10	[54]
4, 4'-DDD	NR	0.026	[53]
	0.32	0.11	[54]
4, 4'-DDT	0.2–7.6	0.074	[52]
	ND	0.01	[51]
	0.63	0.17	[54]
	4.87 ± 1.45	0.029	[53]
Methoxychlor	ND	NR	[59]
	NR	0.024	[53]
	1.71-3.25	0.09	[51]
Chlordane	0.15	0.03	This study
Hexachlorobenzene	0.09	0.02	
4, 4'-DDE	0.17	0.03	
4, 4'-DDD	0.032	0.03	
4, 4'-DDT	1.24	0.02	
Profenofos	0.062	0.01	

ND-Not Detected; NR-Not Recorded.
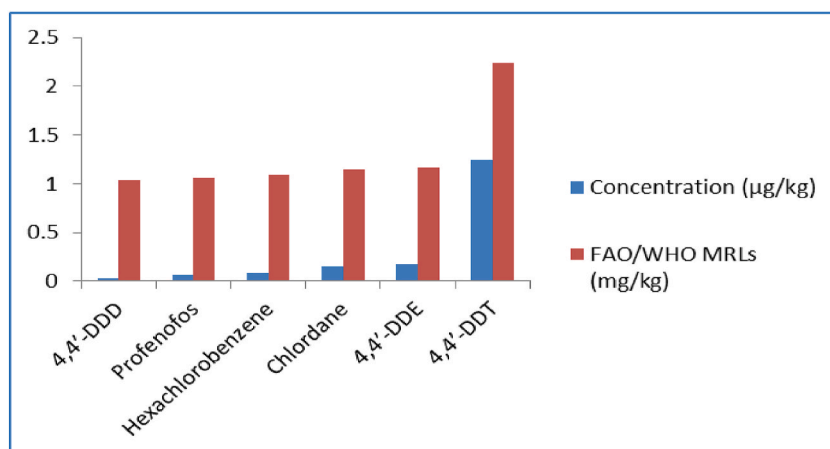
Fig. 2. Pesticide residue detected in tomato samples.

$$\text{LOD} = \frac{3S_{y/x}}{b} = \frac{3}{b}\sqrt{\frac{\sum_i (yi - \hat{y}i)^2}{n - 2}} \tag{1}$$

$$\text{LOQ} = \frac{10S_{y/x}}{b} = \frac{10}{b}\sqrt{\frac{\sum_i (yi - \hat{y}i)^2}{n - 2}} \tag{2}$$

$$\mathbf{y} = \mathbf{b}\mathbf{x} + \mathbf{a} \tag{3}$$

Where $S_{y/x}$ is the standard error of the analytical curve, $\mathbf{y_i} - \hat{\mathbf{y}}_i$ is the y-residuals values of points on the calculated regression line corresponding to the individual **x**-values, **n** is the total number of standard concentration prepared, **y** is the detector response (signal), **x** is the concentration of standard, **b** is the slope of the line and **a** is an intercept on the y-axis.

3.3. Quantitation of pesticides residue in tomato samples

The validated method was applied to tomato samples for analysis of pesticides. A triplicate analysis made done on five different composite samples following procedures described in the materials and methods sections. From the fourteen studied pesticides chlordane, hexachlorobenzene, 4, 4'- DDE, 4, 4'-DDD, 4, 4'-DDT, and profenofos were detected at 0.15, 0.09, 0.17, 0.032, 1.24, and 0.062, µg/kg as depicted in Fig. 2.

Chlordane is a component of technical chlordane that is recognized as an endocrine-disrupting chemical (EDC) in the Stockholm Convention on Persistent Organic Pollutants and can affect the biosynthesis, metabolism, or action of hormones, resulting in imbalanced hormone function [40]. Immensely lipophilic compounds may be transformed into more noxious and dogged chemicals that are deposited in adipose tissue, posing a menace to the human body, including the make-up of adipose tissue responsible for weight regulation [41]. Moreover, chlordane is categorized as a tenacious organic contaminant, as it causes metabolic ailments, comprising obesity [42]. The use of Hexachlorobenzene (HCB) is banned in most countries, however, substantial amounts are being released into the environment [43]. It was also used as a fungicide in the past times. HCB was categorized as possibly a carcinogenic chemical to humans as it disrupts the endocrine system in the thyroid, mammary gland, and uterus [44]. Transfer processes like surface runoff or percolation can bring profenofos, an endocrine-disrupting chemical to aquatic ecosystems [45].

4, 4'-DDT is a chlorinated hydrocarbon insecticide, that was extensively used in the 20th century, even though most countries banned it due to its highly lipophilic nature and very stable characteristics. DDT is mainly metabolically converted into 4, 4'-DDE, and is present ubiquitously in the environment, including food [46]. Despite the banning of DDT, there are evidences that it is purposely applied in fighting vectors, particularly in malaria-endemic regions in Africa. Proper monitoring systems should be settled and well-documented. DDT, an organochlorine pesticide, tolerates degradation in the environment and hence needs long-term monitoring in environmental samples [47].

Ravi et al. has determined the levels of profenofos. 4,4 DDE and hexachlorobenzene in tomato samples to be 0.008 mg/kg, 0.006 mg/kg - 1.09 mg/kg, and 0.004 mg/kg - 0.007 mg/kg, respectively using GC-MS [48] while Jallow et al. found 0.02–0.39 mg/kg and LOD values of 0.0018–0.0021 mg/kg for profenofos with same sample preparation and detection system [49]. In another study involving analysis of tomato matrix effect in pesticide residue quantification through QuEChERS and single quadrupole GC/MS, a 0.02 mg/kg 4, 4-DDE was determined with LOD value of 0.005 mg/kg [50].

Tamene et al. [51] determined the concentrations of some organophosphate and organochlorine pesticides in tomato, potato, and pineapple samples from selected farmlands of Jimma and Kefa Zones, Southwest Ethiopia. They use QuEChERS procedure, AOAC-2007, for extraction of the pesticides from the samples before quantifications by a gas GC-ECD. 4, 4'-DDE was detected at 1.20–1.64 µg/kg, a value higher than the present study, and DDT was not detected. A very high level of 4, 4'-DDE (300–3200 µg/kg) was obtained by Ref. [52] in tomato samples collected from the central valley of Ethiopia but a lower level (1.43 ± 0.15 µg/kg) by Ref. [53]. In a study conducted by Hasan et al. [53] on the detection of organochlorine pesticides in vegetables and fruits from Dhaka, Bangladesh, chlordane was detected at 2.09 ± 0.27 µg/kg in tomato samples while a concentration of 1.02 µg/kg, 5.4 µg/kg and 0.32 µg/kg were found for chlordane, hexachlorobenzene and 4, 4'- DDD, respectively in the same matrix by Ref. [54]. All values are higher than the result of the two analytes in the present study.

The concentration of 4, 4'- DDT was 0.2–7.6 µg/kg in tomato samples from the central rift valley of Ethiopia [52], a value that includes the present result while 0.63 µg/kg and 4.87 ± 1.45 µg/kg were obtained by Refs. [53,54], respectively. DDT mixtures mostly comprise p, p'-DDT (75%), 2, 4' - DDT (15%), 4, 4'- DDE (5%), and numerous additional trace metabolites [55,56]. Usually, 4, 4'-DDT can be dechlorinated into 4, 4'-DDE under aerobic environments and reduced to 4, 4'-DDD under anaerobic conditions [57]. The isomer ratios of various organochlorine pesticides can give a clue whether they are being currently applied or their source is from degradation products used in the past. If the ratio of 4, 4'-DDT to its metabolic products exceeds 1, it is an indicator of current use while a ratio of less than 1 shows its past practice in the environment [54]. Since the ratio of $W_{4,\ 4'\text{-DDT}}/W_{4,\ 4'\text{-DDE}}$ is 7, it designates that DDT is currently being used in the study area.

FAO/WHO recommends 0.02, 3, 3.5, 3.5, 3.5, and 0.07 mg/kg as maximum residue limits for chlordane, hexachlorobenzene, 4, 4'-DDE, 4, 4'-DDD, 4, 4'- DDT and profenofos, respectively [60] and hence are not a threat. However; the presence of these toxic chemicals in tomatoes signals product pollution and needs further studies with other non-considered pesticides, too.

4. Conclusion

Pesticide residue analysis in tomato fruit samples was done based on a validated method employing parameters like recovery (%), linearity, the limit of detection, the limit of quantitation, and precision. Dimethoate, Profenofos, Chlordane, Endosulfan I, Endosulfan II, α-Lindane, Hexachlorobenzene, Heptachlor, Aldrin, Heptachlor epoxide, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, and Methoxychlor analysis in tomatoes fruit samples were done employing QuEChERS sample preparation procedure with d-SPE cleanup and GC-MS detection system. From the fourteen studied pesticides chlordane, hexachlorobenzene, 4, 4'-DDE, 4,4'-DDD, 4,4'-DDT, and profenofos were detected 0.15, 0.09,0.17, 0.032, 1.24, and 0.062 μg/kg, respectively. The values of detected analytes fall in the acceptable range of FAO/WHO [60]. Moreover, the developed method has shown better LODs than other reported works of literature for different pesticides [51–54].

Despite the non-detectability of the studied pesticides in fresh tomato samples except chlordane, hexachlorobenzene, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT, and profenofos, thorough study with source specified and a large number of samples should be done to reach a more generalized result regarding the pollution status of tomatoes in the study area. Moreover, the presence of those detected analytes in lower levels cannot be undermined as it is capable of retaining in environmental samples for decades [47]. Since the ratio of $W_{4, 4'\text{-DDT}}/W_{4, 4'\text{-DDE}}$ is 7 it indicates that DDT is currently being used in the study area. Therefore public awareness on pesticide use, health effects, good agricultural practices that minimize pesticide pollution and management need to be worked on by concerned bodies. There should also be nationally strict rules and regulations on pesticide use, management, and maximum residue limits.

Author contribution statement

Abiyot Kelecha Geleta, Kokob Teshome Wondimu: 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 included in article/supplementary material/referenced in article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.heliyon.2023.e14121.

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