Impact of QuEChERS and GC-MS/MSTQD as MultiresiduesTechniques for Determination of 74 Pesticides in Olive Farm Soil

Abstract

The extraction and analytical multiresidue method, has been developed and validated for quantification of trace levels of 74 pesticide belong to different chemical groups in organic and conventional Olive farm soil samples (Old, medial and new olive farms which is 25, 15 and 5 years respectively). Soil samples collected from Al-Jouf Province, Saudi Arabia, and extracted by Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) and analyzed by Gas Chromatography Mass Spectrometry Triple Quadrupole (GC-MS/MSTQD). The method reveals that experimental results were highly satisfactory in respect of various analytical parameters such as linearity, recovery and precision especially with the tested soil samples which ~~is~~are complex matrixes, preparation is a critical step, and one that is usually expensive, time-consuming, and labor intensive. The limit of detection (LOD) and limit of quantification (LOQ) for the analyzed pesticides were in the range of 1.01-13.91 µg kg^{-1} and 3.02 - 29.15 µg kg^{-1}, respectively. Pesticide recoveries form spiked soil samples with different pesticides ranged from 65.5 to 111.7 %. The proposed method featured good sensitivity, pesticide quantification limits were low enough, and the precision, expressed as relative standard deviation, ranged from 0.29 to 13.32%. Pesticide residues beingdetected by applying the modified QuEChERS and GCMSMSTQD method, the levels were ranged from 43.00 to 2.00 µg kg^{-1} for 18 different pesticides, 1.99 to 1.00 µg/kg^{-1} for 16 different pesticides, 0.99 to 0.50 µg/kg^{-1} for 12 different pesticides and lower than 0.50 µg kg^{-1} for 28 different pesticide residues. The proposed QuEChERS and GC-MS/MSTQD method were applied successfully for the residues extraction and determination the 74 pesticides.

Keywords

Multiresidue, Pesticide residues, Organic farming, Conventional farming, olive farm soil, QuEChERS and GC-MS/MSTQD.

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Introduction

Pesticides are widely used in agriculture to protect crops, control the insects, and improve efficiency of food production. Due to the wide range of pesticides used in agriculture, the development of fast and simple multi-residue methods that simultaneously determine a wide range of different pesticides is essential. One of the most widely used multi-residue methodologies is the Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) approach. This offers many advantages including speed, cost, ease of use, good performance characteristics and wide applicability range (Pszczolińska, and Michel, 2016).

Due to the low concentration levels of soil pollutants such as pesticides and other substances, sample preparation step is needed to determine the type and quantity of such compounds (Caldas, et al., 2011; Wang, et al., 2012 and AOAC, 20117) and to avoid interferences and improve the sensitivity of the method. To remove contaminants from soil samples, a technique strong enough to extract bound pesticide residues in short time is necessary (Pinto et., al 2011 and Rashid et al., 2010).

The QuEChERS approach is based on a salting-out extraction with a solvent (mainly acetonitrile, ACN) followed by a dispersive solid phase extraction (d-SPE). QuEChERS method is very flexible, modifiable, and is growing in popularity due to all the benefits described by its effectiveness is dependent on the analytic properties, matrix composition, equipment, and analytical technique availability (Pinto, et al., 2010; Caldas, et al., 2011; Wang et al., 2012).

Soil samples are complex matrixes; therefore, soil sample preparation is a critical step, and one that is usually expensive, time-consuming, and labor intensive. The (QuEChERS) method, originally developed for the determination of pesticides in fruits and vegetables, recently modified and adopted for the analysis of pesticides in soil (Pszczolińska, and Michel, 2016, Brondi et al., 2011 and Fernandes, et al., 2013) was employed in this study. El-Saeid, et al., (2015) studied the levels of pesticide residues in two types of farmland soils, sandy and clay soils following different farming practices conventional and organic were taken from different depths of 10 and 20cm. Samples were prepared for extraction and were extracted

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using acetone: hexane mixture (1:1) and cleanup was performed using florisil column. Clean extracts weresubjected to pesticide residues determination (a total of 86) belonging to different chemical and action groups using hyphenated GC-MS. Recovery, linearity and experimental limit of detection (LOD) were performed. In case of sandy conventional farmland soil, the detected organochlorines (OCPs) pesticides were 7 or seven, while the organophosphorus insecticides included four compounds. For herbicides two compounds were detected i.e. linuron and Amitraz. As for the frequency of the detected pesticide residues, it was found that the most frequent were endosulfan I, chlorpyrifos-methyl, P,P-DDE, amitraz, fenthion, P,P-DDD, linuron, dimethoate, lindane, dieldrin, O,P-DDD, pirimiphos-methyl, alfa-BHC and aldrin. Also, it was observed that the detected pesticides were lindane, *P,P*-DDE, *O,P*-DDD,*P,P*-DDD, mirex, dieldrin and aldrin as a OCPs. It is clear that the highest amounts of OCPs residues distribution were especially at 20 cm followed by 10 cm (0.273 and 0.235 ppm.), while the numbers of detection pesticide residues at 20 cm depth more than 10cm were 23 and 15 numbers, respectively.

In this study, modified QuEChERS techniques used for the extraction and clean-up procedure followed by GCMSTQD for the analysis of several pesticide residues in soil samples collected form Olive cultivated under conventional and organic farming.

Material and Methods

Standards and Reagents

Pesticides internal, calibration and injection standards with declared 99.9% purity, were purchased from Accu Standard, 153 Inc., New Haven, CT, USA as individual or mixture standards at a concentration of 100-200µg/mL. All internal standards are ^{13}C 12-labelled, the use of ^{13}C-labelled compound is preferable because the analysis can be quantified without clean-up. (Maestroni et al., 2000; Maestroni 2002). All solvents (Methanol, dichloromethane and acetonitrile) used for the extraction and analysis procedures of pesticides were residue-analysis grade 99.9 % purity and obtained from Fisher Scientific (Fair Lawn, NJ, USA). QuEChERS kits were purchased from Phenomenex, Madrid Avenue, Torrance, CA, USA.

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Samples preparation and Extraction

First, weigh 10 g soil sample (≥70% H_2O content) into a 50 mL centrifuge tube. Alternatively, weigh 3 g air-dried soil sample into a 50 mL tube and add 7 mL H_2O, vortex briefly, and allow to hydrate for 30 minutes. Then, add 10 mL of acetonitrile to each sample. Shake (manually or mechanically) or vortex samples for 5 minutes to extract pesticides. (In this study a SpexSamplePrep Geno/Grinder 2010 operated at 1500 rpm was used). After that, add the contents of an ECQUEU750CT-MP (citrate salts) Mylar pouch to each centrifuge tube. Immediately shake samples for at least 2 minutes and centrifuge for 5 minutes at ≥ 3500 rcf.

Sample Cleanup

Transfer a 1 mL aliquot of supernatant to a 2 mL CUMPSC18CT (MgSO4, PSA, C18) dSPE tube. Vortex samples for 0.5–1 min. Centrifuge for 2 min at high rcf (e.g. ≥ 5000). Filter purified supernatant through a 0.2 μm syringe filter directly into a sample vial. Finally, the samples were analyzed by GC-MS/MSTQD.

Analysis by GCMSMSTSQ 8000/SRM

All measurements have been carried out using the latest Thermo Scientific™ TSQ 8000™ triple quadrupole GC-MS/MS system equipped with the Thermo Scientific™ TRACE™ 1310 GC with SSL Instant Connect™ SSL module and Thermo Scientific™ TriPlus™ RSH auto sampler. Injection mode was spiltless, Splitless Time 1.0 min GC Column TR™ 5 MS, 30 m × 0.25 mm × 0.25 μm, carrier gas He (99.999 %, flow rate 1.2 mL/min, constant flow, temperature program 100 °C, 1 min; 10 °C/min to 160 °C, 4 min and 10 °C/min to 250 °C, 2 min, transfer line temperature 280 °C, total analysis time 22.4 min, TriPlus RSH Autosampler Injection volume 1 μL. Ionization mode EI, 70 eV, Ion source temperature 250 °C, scan mode SRM using timed SRM SRM transition setup automatically build-up by AutoSRM software. Transitions conditions are shown in (Table 1).

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128 Table 1: GCMSMSTQD 8000 SRM Instrumental conditions

GC Trace Ultra Conditions		TSQ Quantum MS/MS Conditions	
Column	TR-Pesticide 30 m × 0.25 mm × 0.25 µm	Operating mode	Selected Reaction Monitoring (SRM)
Injector	Splitless	Ionization mode	EI
Injected volume	1 µL	Electron energy	70 eV
Injector temperature	225 °C	Emission current	50 µA
Carrier gas	Helium, 1.2mL/min	Q1/Q3 resolution	0.7 u (FWHM)
Oven program	80 °C hold 1 min 15 °C/min to 160 °C hold 1 min 2.2 °C/min to 230 °C hold 1 min 5 °C/min to 290 °C hold 5 min Run Time 57.15 min	Collision gas	Argon
Transfer line temperature	280 °C	Collision gas pressure	1 mTorr
		Polarity	Positive

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Method performance

Accuracy and precision of the method: 4 replicates of blank water sample spiked with the pesticide standards. Limit of detection: Instrument Detection Limit (IDL), Sample Detection Limit (SDL), Method Detection Limit, accuracy and precision

QAQC Strategies

Quality control samples ~~was~~ being prepared and analyzed duplicate sample, blank and spiked, and/or Certified Reference material CRM was prepared for this purpose and processed with each batch (5-10 samples) of sample. ASE and GCMS or GCMSMS TSQ 8000 method limit of detection (LOD) and Limit of Quantification (LQD), repeatability, reproducibility, accuracy and precession also were determined for each compound in the groups of PAHs and Pesticides.

Results and Discussion

QuEChERS and GC MS/MSTQD for analysis of 74 pesticides.

Simple and rapid method based on QuEChERS extraction and GCMSMSTQD for determination of 74 of different groups of pesticides in soil samples. Retention time, LOD, LOQ, recovery % and target mass of SRM scanning mode was determined as showmen in table (1). The results clearly reflect the developed QuEChERS method offers an efficient, cost effective, and easy sample preparation procedure for the determination of 74 substances or pesticides in soil samples.

Recovery % ranged from 65.5 to 111.7 %., the limit of detection (LOD) and limit of quantification (LOQ) for the analyzed pesticides were in the range of 1.01-13.35 µg kg^{-1} and 3.02 - 29.15 µg kg^{-1}, respectively. The proposed method featured good sensitivity, pesticide quantification limits were low enough, and the precision, expressed as relative standard deviation, ranged from 0.29 to 13.3%.

The calibration curves were linear over wide concentration ranges with correlation coefficients (r2) 0.5092 to 0.9899 for all tested pesticides. In addition, the SRM chromatograms demonstrated high selectivity with no significant interferences observed and an excellent signal/noise ratio (> 5:1) for all tested pesticides as showmen in (Figure 1).

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161 Table (2) Parameters of retention time, LOD, LOQ, recovery % and target mass of SRM scanning
162 mode.

Name	RT	Mass	Product mass	Collision Energy	LOQ	LOD	r^2	Recovery %	SD
Biphenyl	14.82	152	126	23	20.12	6.71	0.7134	108.60	6.32
Methacrifos	17.8	240	180	10	15.20	5.07	0.8379	98.21	6.46
Chloroneb	18.09	206	191	10	19.67	6.56	0.9522	100.42	12.08
Tecnazene	20.86	261	203	13	11.57	3.86	0.9848	104.02	4.98
Propachlor	20.97	120	77	19	8.14	2.71	0.9899	104.94	4.77
Cycloate	21.44	154	83	8	8.00	2.67	0.9905	111.73	3.76
Ethalfluralin	22.01	276	202	15	10.35	3.45	0.9848	113.32	9.52
Trifluralin	22.38	306	160	23	13.92	4.64	0.9760	106.95	7.46
Benfluralin	22.47	292	160	20	11.62	3.87	0.9816	111.04	4.67
Sulfotep	22.59	202	146	10	10.94	3.65	0.9806	110.87	10.89
Diallate	22.78	234	150	18	8.82	2.94	0.9650	86.56	7.30
Alph-BCH	23.04	181	145	13	21.32	10.44	0.8433	104.37	7.45
HCB	23.33	249	214	14	18.70	6.23	0.9382	103.88	0.35
Atrazine	23.94	200	122	10	11.84	3.95	0.9643	108.07	6.52
Terbufos	24.42	231	129	23	15.79	5.26	0.9570	96.64	8.69
Profluraline	24.48	318	199	17	13.67	4.56	0.9688	110.12	7.76
Fenofos	24.56	137	109	6	11.17	3.72	0.9813	110.32	4.49
Diazinone	24.81	137	84	12	21.73	13.91	0.9465	109.28	5.83
Fluchloralin	24.94	264	160	15	16.10	5.37	0.9535	106.12	5.52
Disulfoton	24.99	153	97	12	12.19	4.06	0.9729	87.14	6.75
Tefluthrin	25.14	177	127	15	4.33	1.44	0.9963	100.77	10.39
Triallate	25.28	270	186	18	18.68	6.23	0.9094	89.40	5.74
Endosulfan ether	25.73	272	237	10	24.04	13.35	0.9725	101.44	3.00
Pentachloroaniline	25.92	263	192	20	17.41	5.80	0.9365	102.47	0.29
Alachlor	26.31	146	118	8	17.41	5.80	0.9284	104.52	8.23
Vinclozolin	26.38	285	212	12	15.78	5.26	0.9633	75.14	1.30
Cypermethrin	26.45	163	91	11	15.09	5.03	0.9574	103.94	9.13
Heptachlor	26.62	100	65	12	21.00	11.33	0.8841	102.38	2.75
Acetochlor	26.72	174	146	12	15.56	5.19	0.9497	105.31	7.41

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Fenchlorfos	26.84	285	240	23	9.91	3.30	0.9462	77.09	1.62
Primiphos methyl	27.22	290	125	20	17.45	10.82	0.5092	103.68	9.61
Pentachlorothioanisole	27.43	296	246	32	7.59	2.53	0.9922	93.27	1.54
Dichlofluanid	27.48	123	77	16	16.27	5.42	0.9311	69.56	12.45
Aldrin	27.66	263	191	35	22.69	12.23	0.9175	109.07	3.96
Chloropyrifos	27.81	314	258	12	25.88	11.96	0.9256	79.07	7.31
Triadimefon	27.9	208	181	10	12.62	4.21	0.9673	99.28	4.66
Primiphos - ethyl	28.35	318	166	12	5.35	1.78	0.9957	78.98	6.84
Isopropalin	28.44	280	238	8	16.73	5.58	0.9363	87.18	5.81
Isodrin	28.53	261	191	28	23.51	7.84	0.9895	74.27	3.63
Pendimethalin	28.72	252	162	10	23.72	10.24	0.5688	108.86	2.438
Heptachlor epoxide	28.81	353	263	13	21.48	8.49	0.7901	87.79	4.15
Tolyfluanid	28.88	240	137	10	23.91	7.97	0.8218	84.75	4.82
Quinalphos	29.04	298	156	8	8.32	2.77	0.9896	81.76	2.40
Procymidone	29.22	283	67	28	10.94	3.65	0.9655	97.83	1.65
Chlordane- Cis	29.45	272	237	12	22.64	10.55	0.6677	95.03	1.24
O,P-DDE	29.54	246	176	32	8.96	2.99	0.9908	107.02	2.23
Tetrachlorviphos	29.66	333	109	17	10.77	3.59	0.9805	82.67	8.85
Endosulfan 1	29.79	195	125	19	23.87	10.29	0.9873	96.46	5.35
Chlordane - Trans	29.84	272	237	13	14.96	4.99	0.9394	103.58	2.93
Nonachlor- Trans	29.95	409	302	22	8.88	2.96	0.9077	108.47	7.16
Pretilachlor	30.24	162	132	18	20.69	6.90	0.9806	82.81	7.75
P,P-DDE	30.33	318	248	22	12.72	4.24	0.9478	110.46	8.60
Dieldrin	30.47	279	243	10	15.98	5.33	0.9486	105.50	7.11
O,P-DDD	30.57	235	165	22	16.98	5.66	0.9048	97.09	3.34
Endrin	31.04	279	243	8	21.84	10.61	0.9529	105.27	7.74
Chlorobenzilate	31.09	139	111	12	15.03	5.01	0.8409	65.504	2.99
Endosulfan 2	31.26	241	206	10	18.86	6.29	0.9163	89.98	3.90
P,P-DDD	31.38	235	165	24	8.43	2.81	0.9876	97.47	11.72
O,P-DDT	31.46	235	165	21	10.00	1.61	0.9952	99.12	2.89
Nonachlor - Cis	31.54	272	237	10	29.15	11.72	0.7072	111.22	5.03
Endrin - aldehyde	31.73	345	243	17	28.85	9.62	0.6997	104.519	7.11
Carfetrazone ethyl	31.93	340	312	10	16.56	5.52	0.9348	101.10	11.16

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Methoxychlor olefin	31.99	308	223	30	20.34	6.78	0.8750	103.19	12.33
Endosulfan sulfate	32.28	274	239	12	19.86	12.29	0.6006	92.73	8.71
o, p Methoxychlor	32.49	227	121	12	19.95	6.65	0.7266	91.57	11.92
Resmethrin 1	32.57	123	81	8	15.18	5.06	0.8423	106.47	10.01
Resmethrin 2	32.67	123	81	8	21.08	7.03	0.7226	100.20	8.12
Nitralin	32.9	274	216	6	21.50	8.50	0.7610	109.44	13.07
Bifenthrin	33.31	181	166	10	12.43	4.14	0.9562	106.05	13.32
Bromopropylate	33.39	183	155	12	25.79	8.60	0.7425	75.06	12.44
Endrin ketone	33.44	215	279	8	19.64	10.55	0.6018	85.30	10.80
Methoxychlor	33.55	227	115	50	23.68	12.56	0.6608	88.07	10.38
Tetradifon	34.1	159	111	20	3.02	1.01	0.9861	102.30	10.86
Leptofos	34.35	171	77	18	20.12	6.71	0.7134	108.60	2.48
Mirex	34.7	272	237	15	15.20	5.07	0.8379	90.21	4.35

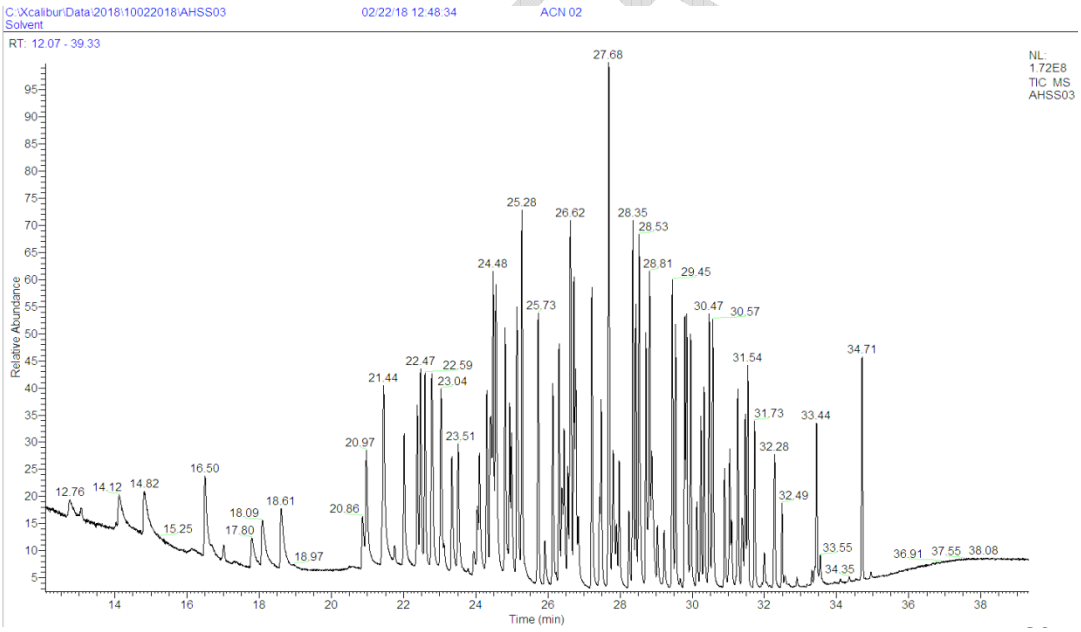

Fig. (1) GC-MSMS TQD Chromatogram obtained from 74 pesticides sample

Case Study: Pesticide residues in conventional and organic farming soil.

Pesticide residues ~~was~~ were detected by applying the modified QuEChERS method: ~~named,~~Chloroneb, Tecnazene, Propachlor, Cycloate, Ethalfluralin, Trifluralin, Beluralin, Sulfotep, Diallate, Alpha BCH, HCB, Atrazine, Terbufos, Profluralin, Fenofos, Diazinon and Fluchloralin and its residue levels ranged from 43.00 to 2.00 $\mu g/kg^{-1}$ in organic and conventional olive farm soil (Fig. 2) extracted by QuEChERS and analyzed by GCMSMSTQD.

Meanwhile, the detected pesticide residues levels (Fig. 3) of Endosulfan ether, Pentachloroaniline, Alachlor, Vinclozolin, Cypermethrin, Heptachlor, Acetochlor, Fenchlorfos, Pirimiphos methyl, Petachlorothioanisole, Dichlofluanid, Aldrin, Chlropyrifos, Triadimefon, Pirimiphos ethyl ranged from 1.99 to 1.00 $\mu g/kg^{-1}$ in organic and conventional olive farm soil extracted by QuEChERS and analyzed by GCMSMSTQD.

Also, Isopropalin, Isodrin, Pendimethalin, Heptachlor epoxide, Tolyfluanid, Quinalphos, Procymidone, cis-Chlorodane, o,p-DDE, Tetrachlorviphos, Endosulfan I, and chlordane-trans was detected in organic and conventional olive farm soil extracted by QuEChERS and analyzed by GCMSMSTQD and ranged from 0.99 to 0.50 $\mu g/kg^{-1}$ (Fig. 4).

Pesticide residues of~~named,~~ Chlordane-trans, Nonachlor-trans, Pretialchlor, p,p-DDE, Dieldrin, o,p-DDD, Endrin, Chlorobenzilate, Endosulfan II, p,p-DDD, o,p-DDT, Nonachlor-cis, Endrin aldehyde, Carfetrazone ethyl, Methoxychlor olefin, Endosulfan sulfate, o,pMethoxychlor, Resmethrin 1, Resmethrin 2, Nitralin, Bifenthrin, Bromopropylate, Endrin_ketone, Methoxychlor, Tetradifon, Leptofos, and Mirex~~was~~ ranged as low as 0.50 $\mu g/kg^{-1}$**.**

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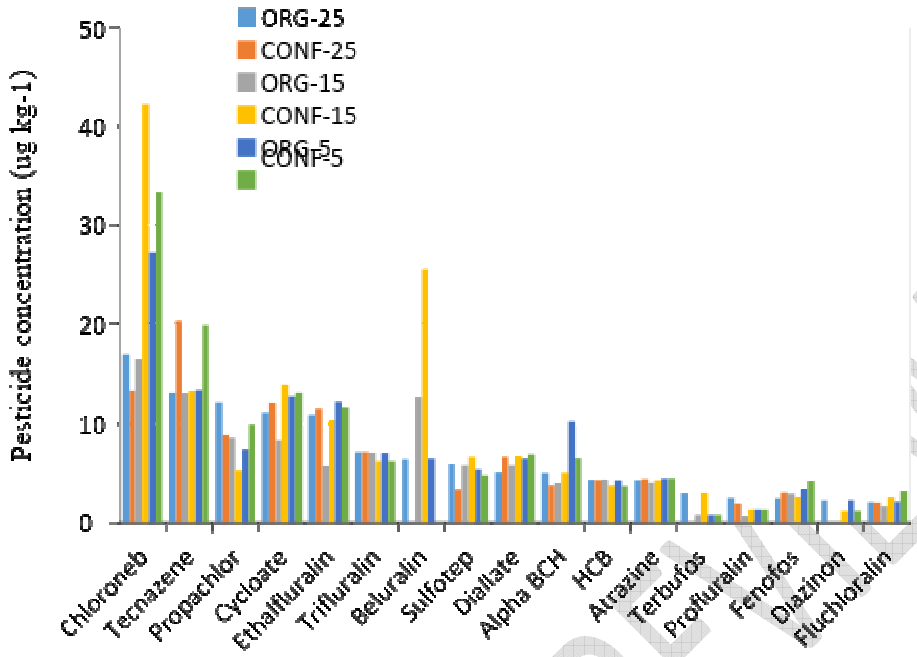

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215 Fig. (2) Pesticide Residues levels (µg kg^{-1} ranged from 43 to 2 ppb in organic and conventional
216 olive farm soil extracted by QuEChERS and analyzed by GCMSMSTQD.

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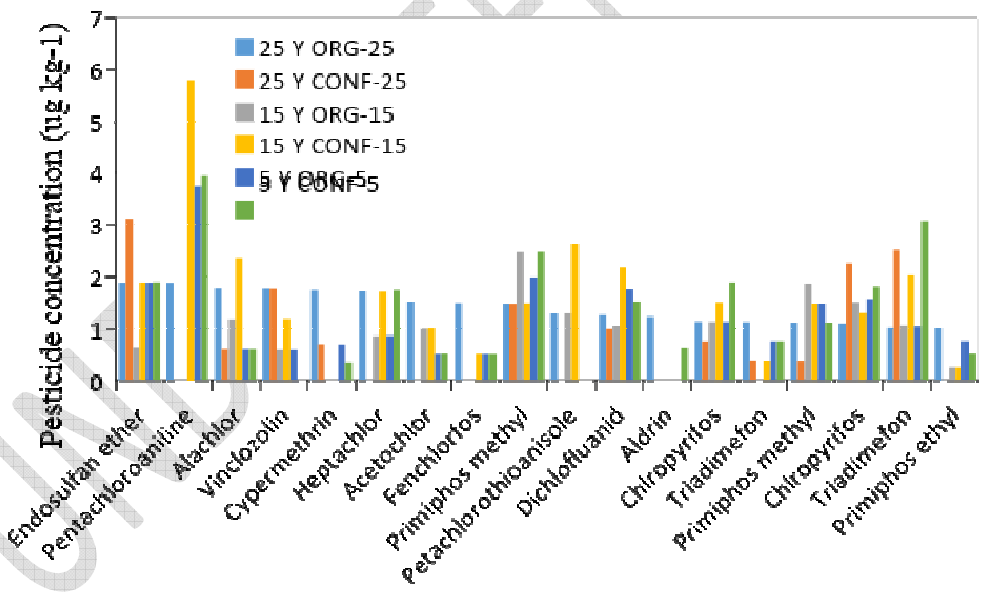

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220 Fig. (3) Pesticide Residues levels (µg kg^{-1}) ranged from 2 to 1 ppb in organic and conventional
221 olive farm soil extracted by QuEChERS and analyzed by GCMSMSTQD.

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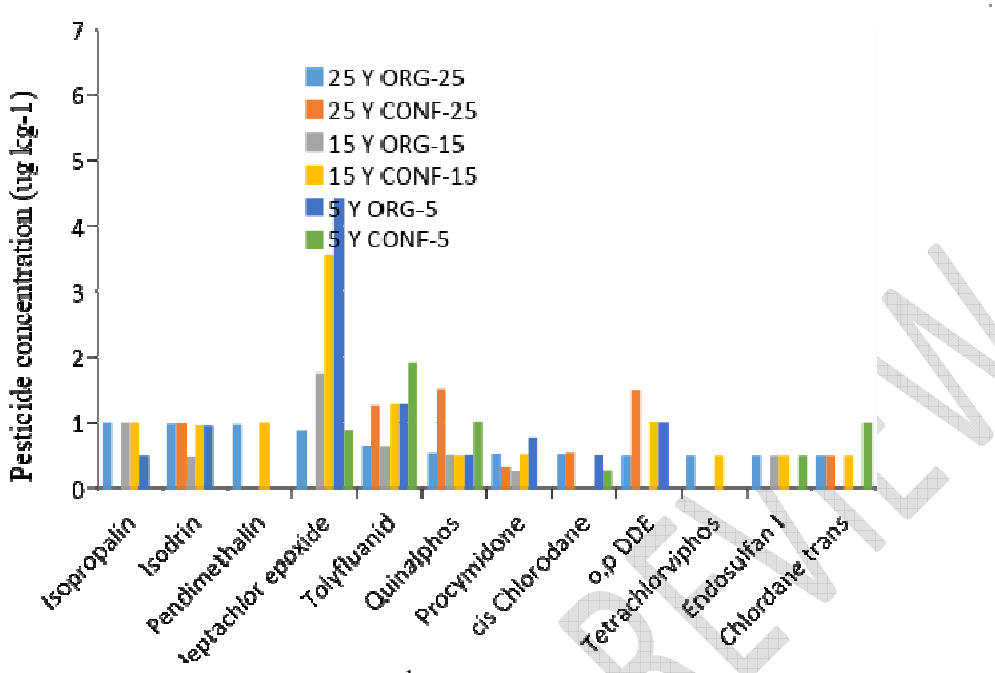

Fig. (4) Pesticide Residues levels (µg kg^{-1}) ranged from 0.5 to 1 ppb in organic and conventional olive farm soil extracted by QuEChERS and analyzed by GCMSMSTQD.

Conclusions

The QuEChERS method is becoming increasingly more popular as a new and robust procedure. QuEChERS-GC/MS/MS multi-residue method described here is a simple, rapid and accurate approach suitable for the monitoring of 74 pesticide residues in old, medial and new olive farms which is 25, 15 and 5 years olive farm soil samples. The proposed method have been validated lowing a reliable determination of the selected compounds with high recoveries. The limit of detection (LOD) and limit of quantification (LOQ) for the analyzed pesticides were in the range of 1.01-13.91 µg kg^{-1} and 3.02 - 29.15 µg kg^{-1}, respectively. Pesticide recoveries form soil samples spiked with pesticides ranged from 65.504 to 111.73 %. The proposed method featured good sensitivity, pesticide quantification limits were low enough, and the precision, expressed as relative standard deviation, ranged from 0.29 to 13.32%. Pesticide residues was detected by applying the modified QuEChERS and GCMSMSTQD method levels was ranged from 43.00 to 2.00 µg kg^{-1} for 18 different pesticides, 1.99 to 1.00 µg kg^{-1} for 16 different pesticides, 0.99 to 0.50 µg kg^{-1} for 12 different pesticides and lower than 0.50 µg

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kg^{-1} for 28 different pesticide residues. QuEChERS provides high quality results with a high sample throughput. Additionally, there is low solvent and glassware consumption, with low work and cost of analysis per sample.

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