J. Int. Environmental Application and Science, Vol. 20(2): 131-139 (2025)
Research Paper

Evaluation of Pesticides in Soil and Dry fruits (Hazelnuts) of Mallakastra Region, Albania

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Received May 24, 2025; Accepted June 09, 2025

Abstract: Dried fruits such as hazelnuts, walnuts, almonds, *etc*. grow naturally in Albania due to suitable climatic conditions. They are widely distributed from coastal to mountainous areas of the country. Recent years the consumption of dried fruits has increased significantly due to the good qualities that these products present for the body. Hazelnuts contain high percentage of vitamins, minerals and antioxidants. Before 2000, dried fruits, including hazelnuts, have been limited on their use (mainly to sweets). Last years, many agricultural lands have been planted with hazelnut fruits due to the economic benefits. For these important food products (dry fruits), analyses of pesticides and other pollutants are important because can directly affect population health. Hazelnut fruits and soil samples were taken in six stations in Mallakastra area. Pesticide analysis was performed in hazelnut fruits according to the EN ISO 15662:2018 Foods of plants origin method which is a multi-residue method for the determination of pesticides using GC/MS/MS and LC/MS/MS techniques. The method allows the simultaneous determination of more than 600 individuals. Sample treatment is based on acetonitrile extraction/partitioning and clean-up by dispersive SPE. The procedure is a modular QUEChERS-method recommended for the analysis of pesticides in samples with lower percentage of water (such as dry fruits). Almost the same procedure was used for treatment of soil samples. Extraction in ultrasound by using acetonitrile and QUECHERS salt for clean-up procedure were used for pesticide analyse from soil samples. It was observed that pesticides were not detected (N.D) or their levels were lower than the limit of defect (LOD < 10 ug/kg) in all analyzed hazelnut samples. Some traces of organochlorine pesticides were found in hazelnut fruits (always below LOD level). The same pesticides were found in soil which could be the main source of pesticides to the fruit. Their presence will not exceed the permitted level for analysed samples but their presence (even in trace level) should encourage the responsible institutions for continuous analysis for both matrices, food products and soil samples.

Keywords: *Dry fruits, Food safety, multi-residue analyse, Soil, Pesticides, GC/MS/MS and LC/MS/MS*

Introduction

Albania has a suitable climate for the growth of many fruit trees including hazelnuts, walnuts, almonds, etc. The suitable climate allows them to grow from coastal areas to mountainous areas. The fruits grown in the country are well-known by their quality due to the autochthonous seeds that are best adapted to the country's climate. Before the 90s, the planting of fruit trees was mainly carried out on poor soils because good soils were mainly used for planting cereals. After the 90s, many agricultural lands (of good categories) were left unplanted due to the fragmentation of lands in small fields (private one) and the emigration of population from rural areas. After the 2000s, the situation changed because many immigrants returned to invest in their homeland and many of the agricultural lands were planted by fruit trees (mainly olives, apples, grapes, etc). Recent years the consumption of dried fruits plays an important role in a balanced diet due to the high content of vitamins, minerals and antioxidants. Dried fruits, including hazelnuts, have been part of Albanian diet since ancient times, but their use was limited

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mainly to sweets. Hazelnut is a tree that is found almost throughout the territory of Albania, mainly in its wild (natural) form. In recent years (after 2010), hazelnuts and other nuts (walnuts, chestnuts, almonds, etc.) are being cultivated by farmers in many plantations in all Albanian territory, but many of these plantations have been established in agricultural areas where pesticides have been used frequently in the past (Nuro et al, 2007). This was the reason why the level of pesticides in fruit and soil samples must be evaluated. In general, pesticides are not directly applied to hazelnuts, but accumulation processes (from pesticides accumulated in soil) can affect the presence of pesticides to fruits. In September 2024, hazelnut samples were taken from different plantations in Mallakastra area. Samples were selected in this region because Mallakastra is part of Myzeqeja Field, which is the main agricultural area on the country. In this field the application of pesticides has been very frequent from 1946 to 1992 because there has developed a large scale of agricultural activity. Although after the 1990s this activity declined, it revived after the 2000s. Even today this area is one of the most important agricultural areas of the country where large quantities of cereals, fruits, vegetables, medicinal plants, etc. are grown. Also, in this area, the largest hazelnut plantations (and other trees) can be found.

The hazel tree includes any of the nuts deriving from species of the genus Corylus, especially the nuts of the species *Corylus avellana*. Wild hazelnuts are traditionally grown as multi-trunk trees where the rootstock is formed by the variety itself. To enhance the possibility for mechanization and to prevent suckering, a single-trunk tree can be formed by grafting process. Hazelnuts are used as secondary food, mostly as a snack food, in baking and desserts but many studies have shown that their fruits contain high amounts of protein, dietary fibre, vitamin E, iron, thiamine, phosphorus, manganese, and magnesium (Gruine & Correia, 2020; Santillo *et al*, 2004). Also, they contain B vitamins have appreciable content, significant amounts are vitamin K (low levels but necessary for the body), calcium, zinc, and potassium. Hazelnuts are a rich source of dietary fat. The fat components are monounsaturated fat as oleic acid (75% of total), polyunsaturated fat mainly as linoleic acid (13% of total), and saturated fat, mainly as palmitic acid and stearic acid (together, 7% of total) (Gruine & Correia, 2020). Its nutritional value and market demand for this product have made hazelnuts one of the fruits whose production has increased several times higher than their production/consumption before the year 2000. This important fruit should receive the attention of the authorities regarding its quality. Although pesticides are not applied directly to the hazelnut fruit and moreover it is protected by the peel that surrounds it, the transfer of pesticides from the roots to the fruit may be possible (Skibniewska and Smoczynski, 2000). When soils contain high levels of pesticides, they can be the main source of contamination of the fruit with pesticides or other pollutants (Santillo *et al,* 2004; Sefiloglu *et al*, 2021, Silva *et al*, 2019; Wilhelm *et al*, 2002).

Material and Methods

Study Area and Sampling Stations

Hazelnut fruits and soil samples were taken in September 2024 in six different plantations of Mallakastra area (Fig. 1). In this area there is many hazelnut, walnut and almond plantations. This area is included in the Myzeqe Field which is the largest agricultural area in the country. In this agricultural area before the 90s, mainly cereals and vegetables were planted, and pesticides were also constantly used frequently. After the 90s the situation changed due to the division of lands into small plots and the emigration processes of the population. Many lands were not planted and turned into barren (Nuro, 2007). After the 2000s many of these lands were replanted mainly with fruit trees such as olives, apples, grapes, walnuts, almonds and hazelnuts. Their planting in agricultural lands where pesticides had been used earlier prompted us to think about a study both in the soil and in dried fruits to observe the possibility of their passage and the risk to the population (Skibniewska & Smoczynski, 2000; Santillo *et al*, 2004; Sefiloglu *et al*, 2021, Silva *et al*, 2019). Hazelnut samples were dried and closed to the plastic bags. Soil samples were taken at a depth of 0 – 50 cm in the same plantations where the hazelnut samples were taken. The soil samples were left to air dry initially and then ground in a porcelain mortar. They were sieved and only the 63-micron fraction was taken for analysis which has a porosity suitable for pesticide absorption. They were stored in a dry place before their analyses.

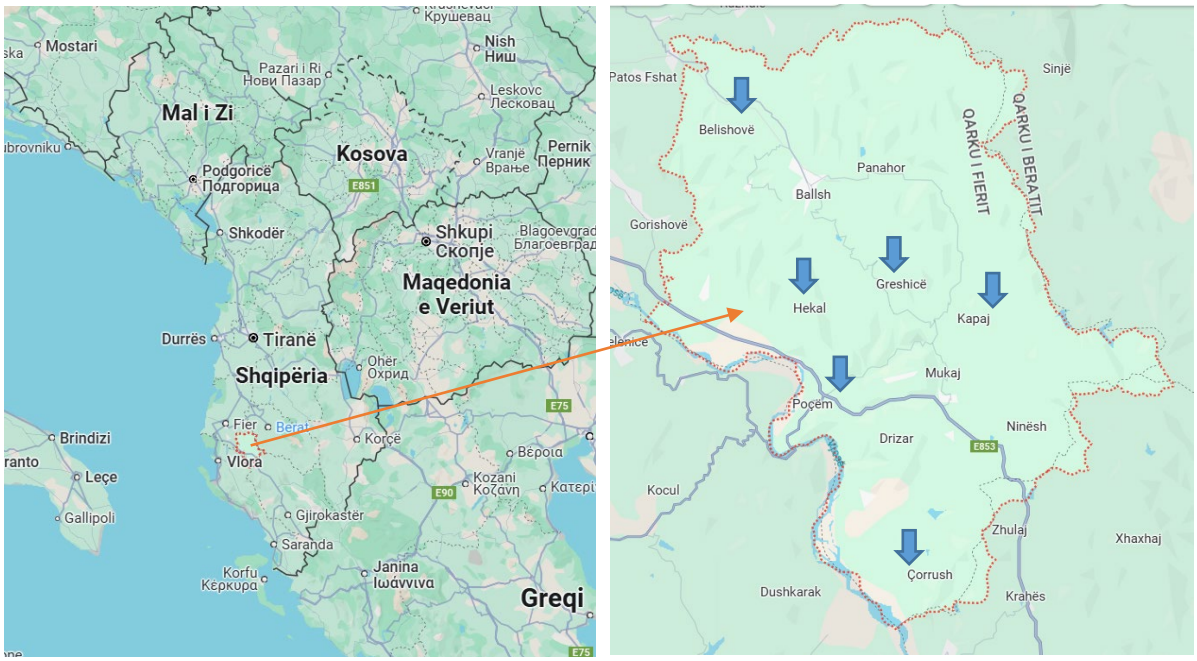

Figure 1. Sampling sites at Mallakastra area, Albania

Sample treatment for multi-residue analyses of pesticides in dry fruits

Pesticide analysis was performed in hazelnut fruits according to the EN ISO 15662:2018. This is a method for foods of plants origin which is a multi-residue method for the determination of pesticides using GC/MS/MS and LC/MS/MS techniques. The method allows the simultaneous determination of more than 600 individuals in a run (in both techniques). Sample treatment is based on acetonitrile extraction/partitioning and clean-up by dispersive SPE. The fruit samples were stored at +4ºC before analysis. The samples were left for about 1 hour at room temperature before analysis. Hazelnut fruits were previously ground in a mill 2 gram of ground dry fruit sample were taken in a Teflon tube. 8 ml of MilliQ distilled water are added and mixed in a vortex. It was left to stand for 10 minutes and then 10 ml of ACN were added to it. It was mixed again in a vortex and after being left to stand for 2 minutes. After that it was treated with citrate tube salt (Quercher 1). The container was placed on an automatic shaker for 5 minutes and then in a centrifuge at 8000 Rpm, at 4oC, for 5 minutes. A quantity of 6 ml of supernatant were taken and transferred to a PSA tube with C18 (Quercher 2) and mixed to a vortex (2 min). After this, the centrifuge was used again at 8000 Rpm, for 5 minutes, at +4ºC. The supernatant was filtered through a 0.45 um filter using a syringe and collected in two different chromatographic vials. The vial to be analysed in the LC/MS/MS technique was injected directly while the vial to be injected into the GC/MS/MS apparatus was first dried completely under a nitrogen stream and then recovered with 1 ml of the mixture Ethyl acetate/n-Hexane (3/7). In addition, the calibration curve were built for pesticides in concentrations of 1, 5, 10, 25 and 50 ug/l for both devices (Silva et al, 2019; Nshimiyimana et al, 2014; Mahdavi et al, 2021; Lozowicka et al, 2017; Homazava et al, 2014; Hvezdova et al, 2018, Accosta-Dacal et al, 2021; Asensio-Ramos et al, 2010; Beltran et al, 2000).

Treatment procedure of soil samples for analyses of pesticides

Soil samples were sieved and fraction of 63 micron was considered for the study. The treatment procedure of soil sample was almost the same with treatment of dry fruit samples by using modular acetonitrile (for extraction) and modular SPE (Quercher salts) for clan-up procedure. The analysis allows complete extraction of pesticides from soil samples and SPE removes compounds that may interfere in the pesticide analysis such as fats, carbohydrates or other macromolecules. 5 grams of soil (sieved sample) were taken in a Teflon tube. 8 ml of MilliQ distilled water are added and mixed in a vortex. It was left to stand for 10 minutes and then 10 ml of ACN were added to it. It was mixed again in a vortex and after being left to stand for 2 minutes. After that it was treated with citrate tube salt (Quercher 1). The container was placed on an automatic shaker for 5 minutes and then in a centrifuge at 8000 Rpm, at 4ºC, for 5 minutes. A quantity of 6 ml of supernatant were taken and transferred to a

PSA tube with C18 (Quercher 2) and mixed to a vortex (2 min). After this, the centrifuge was used again at 8000 Rpm, for 5 minutes, at +4ºC. The supernatant was filtered through a 0.45 µm filter using a syringe and collected in two different chromatographic vials. The vial to be analyzed in the LC/MS/MS technique was injected directly while the vial to be injected into the GC/MS/MS apparatus was first dried completely under a nitrogen stream and then recovered with 1 ml of the mixture Ethyl acetate/n-Hexane (3/7). The same calibration curves were used for both devices (Silva *et al,* 2019; Nshimiyimana *et al*, 2014; Mahdavi *et al*, 2021; Lozowicka *et al*, 2017; Homazava *et al*, 2014; Hvezdova *et al*, 2018, Accosta-Dacal et al, 2021; Asensio-Ramos et al, 2010; Beltran *et al*, 2000).

GC/MS/MS analyses of pesticides

For the analysis of pesticides, the Agilent GC/MS/MS-7000D GC/TQ instrument was used. Also, the instruments were equipped with an auto-sampler and a vacuum system. The BP5-Ms capillary column with dimensions of 30 m x 0.25 mm x 0.25 um I.D. was used for pesticide separation. The qualitative/quantitative method of pesticide determination with GC/MS/MS was optimized before the analysis of both samples (dry fruits and soil samples). The parameters of the GC/MS/MS apparatus were evaluated before analyses of samples. Qualitative analytical data for each pesticide (222 individuals, see Table 1) were provided by the retention time (RT) and by the selection of two specific ions (qualitative and quantitative ions) for everyone. The selection of ions is based on the pesticide database and the NIST spectral library. Quantitative analysis of pesticides was performed using the internal standard technique (ISTD) where triphenyl phosphate (TPP with a concentration of 10 ppb). Spectral and numerical data for the sample were generated by the "Mass Hunter" software provided by Agilent for this instrument model (Silva *et al*, 2019; Nshimiyimana *et al*, 2014; Mahdavi *et al*, 2021; Lozowicka *et al,* 2017; Homazava *et al*, 2014; Hvezdova *et al,* 2018, Accosta-Dacal *et al*, 2021).

LC/MS/MS analyses of pesticides

The Agilent LC/TQ instrument (LC Model 1290/TQ Model 6470) was used for determination of pesticides (425 individuals, see Table 2) in hazelnut and soil samples. Note, that some pesticides were determined in both apparatuses. A C18 Zorbax model column (240 x 4 mm) was used for the separation of pesticides in the LC/MS/MS apparatus. Two types of mobile phase were used: Phase A - water with 5 mM sodium formate/formic acid buffer and Phase B - MeOH with 5 mM sodium formate/formic acid buffer. Before analyses, the column was rinsed with a mixture of 25% isopropanol and methanol/water solutions (1/3) to clean the column and the chromatographic system. Qualitative data for each compound were provided by the retention time (RT) and by the selection of two specific ions (one for qualitative and the other for quantitative analyses) for each individual. The selection of ions is based on the pesticide database and the NIST spectral library. The quantitative analysis of pesticides was based in internal standard technique (ISTD) using triphenyl phosphate (TPP at a concentration of 10 ppb). Spectral and numerical data for the sample were generated by the "Mass Hunter" software provided by Agilent for this device model (Silva *et al*, 2019; Nshimiyimana *et al*, 2014; Mahdavi *et al,* 2021; Hvezdova *et al*, 2018, Accosta-Dacal *et al*, 2021).

Results and Discussions

The analysis of pesticides in products dry fruits (samples with low water level) and soil samples from hazelnut plantations of Mallakastra were performed by using GC/MS/MS and LC/MS/MS techniques, based on the EN 15662:2018 method. The method allows the simultaneous determination of more than 600 individuals (646 pesticides and their residues) in a run (in both techniques). Table 1 shown the pesticide list obtain by GC/MS/MS and Table 2 pesticide list analysed by LC/MS/MS. Sample treatment for dry fruits and soil samples is based on acetonitrile extraction/partitioning and clean-up by dispersive SPE. The procedure is a modular QUEChERS-method recommended for the analysis of pesticides (multi-residue) mostly in food samples. The method can be used for other matrices such as soil, sediment, biota, etc., because the extraction of pesticides with acetonitrile (a recommended solvent) and the clan-up procedure performed by QUERChERS salt are appropriate steps for the analyses of pesticides (Silva *et al,* 2019; Nshimiyimana *et al,* 2014; Mahdavi *et al*, 2021; Lozowicka *et al*, 2017; Homazava et al, 2014; Hvezdova et al, 2018, Accosta-Dacal *et al*, 2021).

Table 1. List of pesticides analysed by GC/MS/MS analyse

2, 4-D-Isopropyl	Chlorbufam	Ditalimfos	Ioxynil - Octanoate	Pirimiphos-Ethyl
2,4,5-T-Isobutyl	cis-Chlordane	Edifenphos	Iprodione	Pretilachlor
2,4,5-TP	trans-Chlordane	alpha-Endosulfan	Isazofos	Profenofos
2,4'-DDD	Chlordecone	beta-Endosulfan	Isodrin	Prometon
2,4'-DDE	Chlorfenapyr	Endosulfan-Ether	Isofenphos	Propetamphos
2,4'-DDT	Chlorfenson	Endosulfansulfate	Isopropalin	Prosulfocarb
2,4-D-Methyl	Chlorfluazuron	Endrin	Isopyrazam	Prothiofos
4,4'-DDD	Chlormephos	Endrin aldehide	Leptophos	Pyraclostrobin
4,4'-DDE	Chlorobenzilate	EPN	Mancozeb	Pyraflufen-Ethyl
4,4'-DDT	Chloroneb	Epoxiconazole	MCPA Ethyl	Pyrazophos
Acetochlor	Chloropropylate	Esfenvalerate	MCPA- Methyl	Pyridalyl
Acibenzolar-S-Methyl	Chlorothalonil	Ethalfluralin	MCPA, 1-butyl	Pyroquilon
Aclonifen	Chlorpropham	Ethiofencarb	MCPA, 2 Ethylhexyl	Pyroxsulam
Acrinathrin	Chlorpyrifos_Dursban	Ethiolate	Butotyl-MCPA	Quinalphos
Alachlor	Chlorsulfuron	Etridiazole	MCPP, 1-OCTYL	Quinclorac
Aldrin	Chlorthal-Dimethyl	Etrimfos	MCPP-Methyl	Quintozene
Ametryn	Chlorthion	Fenchlorphos	Mecoprop - 2- Octyl	Sebuthylazine
Amitraz	Chlorthiophos	Fenitrothion	Mecoprop - 2,4,4-Trimethylpentyl	Secbumeton
Ancymidol	Chlozolinate	Fenoxycarb	Mecoprop -2- Butoxyethyl	Simazine
Anthraquinone	Cinidon-Ethyl	Fenpropimorph	Mecoprop-2-Ethylhexyl	Simeconazole
Atraton	Clethodim	Fenson	Methoxychlor	Sulfotep
Atrazine	Crufomate	Fensulfothion	Metiram	Sulprofos
desethyl-Atrazine	Cyanophos	Fenthion	Mirex	Tebupirimfos
Benazolin	Cycloheximide	Fenvalerate	Naled	Tebutam
Benfluralin	Cyfluthrin (SUM)	Fipronil	Nitrofen	Tecnazene
Bensulide	beta-Cyfluthrin	Fipronil- Desulfinyl	Nitrothal-Isopropyl	Tefluthrin
alpha-BHC	lambda-Cyhalothrin	Flamprop-Methyl	Norflurazon, Desmethyl	Terbacil
beta-BHC	Cypermethrin	Fluazifop-P-Butyl	Orthophenylphenol	Terbumeton, Desethyl
delta-BHC	Deltamethrin	Flucarbazone Sodium	Oxadixyl	Tetradifon
gamma-BHC	Demeton O	Fluchloralin	Oxychlordane	Tetramethrin
Bifenox	Demeton-S-Methyl	Flucythrinate	Oxyfluorfen	Tetrasul
Bioallethrin	Demeton-S-Methylsulfone	Fluthiacet-methyl	Paraoxon-Methyl	Thiocyclam-Oxalate
Bioresmethrin	Dialifos	tau-Fluvalinate	Parathion	Thiometon
Biphenyl	Dichlobenil	Folpet	Parathion-Methyl	Thionazin
Bromophos-Ethyl	Dichlofenthion	Fonofos	Pebulate	Tolylfluanide
Bromophos-Methyl	Dichlofluanid	Formothion	Penoxsulam	Transfluthrin
Bromopropylate	Dichlormid	epsilon-HCH	Pentachlorbenzene	Tributylphosphate
Bromoxynil-octanoate	2,6 -Dichlorobenzamide	Heptachlor	Pentachloroaniline	Trichlorfon
Butafenacil	Diclofop-Methyl	cis-Heptachlorepoxid	cis-Permethrin	Trifluralin
Butralin	Dicloran	trans-Heptachlorepoxid	trans-Permethrin	Trinexapac - Ethyl
Captafol	Dicofol	Heptenophos	Perthane	Vamidothion
Captan	Dieldrin	Hexachloro-1,3butadien	Phenothrin	Vinclozolin
Carbophenothion	Diphenylamine	Hexachlorobenzene	Phorate	
Chinomethionat	Dipropetryn	Iodofenphos	Pinoxaden	
Chlorbromuron	Disulfoton	Ioxynil - Methyl	Piperophos	

Table 2. List of pesticides analyzed by LC/MS/MS analyze

2.4.5-T	Cyflufenamid	Fenthion sulfon	Mefenpyr-diethyl	Propham
2.4-D	Cyhalofop-Butyl	Fenthion-Oxonsulfoxide	melathion	Propiconazole
Abamectin	Cymiazol	Fenuron	Mepanipyrim	Propoxur
Acephate	Cymoxanil	Fipronil	Mepronil	Propyzamide (Pronamide)
Acequinocyl	Cyproconazole	Fipronil sulfone	Mesosulfuron-methyl	Proquinazid
Acetamiprid	Cyprodinil	Flamprop-isopropyl	Metaflumizone	Prothioconazole
Acifluorfen	Daimuron	Flazasulfuron	Metalaxyl	Prothioconazole desthio
Alanycarb	Dazomet	Flonicamid	Metamitron	Pymetrozin
Aldicarb sulfoxide	DEET	Florasulam	Metazachlor	Pyracarbolid
Allidochlor	Demeton S	Fluazifop	Metconazole	Pyributicarb
Ametoctradin	Desmedipham	Fluazinam	Methabenzthiazuron	Pyridaben
Amidosulfuron	Desmetryn	Flubendiamide	Methacrifos	Pyridafenthion

Aminocarb	Di-allate	Flucarbazone Sodium	Methamidophos	Pyridat
Amisulbrom	Diazinon	Fludioxonil	Methidathion	Pyrifenox
Anilazine	Dichlorvos	Flufenacet	Methiocarb	Pyrimethanil
Atrazine Desisopropyl	Diclobutrazol	Flumetralin	Methiocarb-sulfoxide	Pyriproxyfen
Avermectin B1a	Dicrotophos	Flumetsulam	Methomyl	Quinalphos
Azaconazole	Diethofencarb	Flumioxazin	Methoprene	Quinclorac
Azamethiphos	. N.N- Diethyl-m-toluamid	Fluometuron	Methoprotryne	Quinmerac
Azinphos-ethyl	Difenoconazole	Fluopicolide	Methoxyfenozide	Quinoclamin
Azinphos-methyl	Difenoxuron	fluopyram	Metobromuron	Quinoxyfen
Azoxystrobin	Diflubenzuron	Fluoxastrobin	Metolachlor	Quizalofop-ethyl
Barban	Diflufenican	Fluquinconazole	Metosulam	Quizalofop-P
Beflubutamid	Dimefox	Fluridone	Metrafenon	Resmethrin
Benalaxyl	Dimefuron	Flurochloridon	Metribuzin	Rotenone
Bendiocarb	Dimepiperate	Fluroxypyr -meptyl	Metsulfuron-methyl	Saflufenacil
Benfuracarb	Dimethachlor	Flurprimidol	Mevinphos	Secbumeton
Benodanil	Dimethenamide	Flusilazole	Mexacarbate	Sethoxydim
Benoxacor	Dimethoate	Flutolanil	Molinate	Silthiofam
Bensulfuron-methyl	Dimethomorph	Flutriafol	Monocrotophos	Simetryn
Bentazone	Dimethylvinphos	Fluxapyroxad	Monuron	Spinetoram
Benthiavalicarb-isopropyl	Dimetilan	Fomesafen	Moxidectin	Spinosad A
Benzoximate	Dimoxystrobin	Foramsulfuron	Myclobutanil	Spinosad D
Benzoylprop-ethyl	Diniconazole	Forchlorfenuron	Napropamide	Spirodiclofen
Bifenazate	Dinitramine	Fosthiazate	Naptalam	Spiromesifen
Bifenthrin	Dinotefuran	Fuberidazol	Neburon	Spirotetramat
Bispyribac	Dioxacarb	Furalaxyl	Nicosulfuron	Spiroxamine
Bitertanol	Diphenamid	Furathiocarb	Nicotine	Sulfadiazole_Ethidimuron
Bixafen	Disulfoton Sulfone	Griseofulvin	Nitenpyram	Sulfallate
Boscalid	Disulfoton-sulfoxid	Halofenozide	Nitralin	Sulfentrazone
Bosclid (Nicobifen)	Diuron	Halosulfuron-methyl	Norflurazon	Sulfosulfuron
Bromacil	dmst	Haloxyfop	Novaluron	Tebuconazole
Bromfenvinphos	Doramectin	Haloxyfop-ethotyl	Nuarimol	Tebufenozid
Bromuconazole	Emamectin - Benzoate	Haloxyfop-methyl	Ofurace	Tebufenpyrad
Bupirimate	Epoxyconazol	Hexaconazole	Omethoat	Tebuthiuron
Buprofezin	Eprinomectin	Hexaflumuron	Omethoate	Teflubenzuron
Butachlor	EPTC	Hexazinone	Orbencarb	Temephos
Butamifos	Esprocarb	Hexythiazox	Oryzalin	Tepraloxydim
Butocarboxim	Etaconazole	Hydramethylnon	Oxadiargyl	Terbufos
Butoxycarboxim	Ethametsulfuron-Methy	Imazalil	Oxadiazon	Terbufos sulfone
Buturon	ethidimuron	Imazamethabenz methyl	Oxamyl	Terbumeton
Butylate	Ethiofencarb sulfone	Imazapyr	Oxasulfuron	Terbuthylazine
Cadusafos	Ethiofencarb sulfoxide	Imazaquin	Oxycarboxin	Terbuthylazine desethyl
Carbaryl	Ethion	Imazethapyr	Paclobutrazol	Terbutryn
Carbendazim	Ethiprole	Imibenconazole	Paraoxon - ethyl	Tetrachlorvinphos (Dietreen T)
Carbetamide	Ethirimol	Imidacloprid	Penconazole	Tetraconazole
Carbofuran	Ethofumesate	Indanofan	Pencycuron	Thiabendazol
Carbosulfan	Ethoprophos	Indoxacarb	Pendimethalin	Thiacloprid
Carboxin	Ethoprophos_Ethoprop	iodosulfuron-methyl sodium	Penthiopyrad	Thiamethoxam
Carfentrazone-ethyl	Ethoxyquin	IOXYNIL	Pethoxamid	Thidiazuron
Carpropamid	Etofenprox	Ipconazole	Phenmedipham	Thiobencarb
Chlorantraniliprole	Etoxazole	Iprobenfos	Phenthoate	Thiodicarb
Chlorfenvinphos	Famoxadone	Iprovalicarb	Phorate sulfone	Thiofanox
Chlorfluazuron	Famphur (Famophos)	Isocarbamide	Phosalone	Thiofanox sulfon
Chloridazon (Pyrazon)	Fenamidon	Isocarbophos	Phosmet	Thiram
Chlorotoluron	Fenamiphos	Isofenphos methyl_1 TS	Phosphamidon	Tolclofos-methyl
Chloroxuron	Fenamiphos sulfone	Isoprocarb	Picloram	Tolylfluanide
chlorpyrifos - ethyl	Fenamiphos sulfoxide	Isoprothiolane	Picolinafen	Tralkoxydim
Chlorpyrifos	Fenarimol	Isoproturon	Picoxystrobin	Tralomethrin
Chlorpyrifos-Oxon	Fenazaquin	Isoxaben	Piperonyl butoxide	Triadimefon
Chlorpyriphos-methyl	Fenbuconazole	Isoxadifen-ethyl	Pirimicarb	Triadimenol
Chlorthiamid	Fenhexamid	Isoxaflutole	Pirimicarb-desmethyl	tri-allate
Cinosulfuron	Fenobucarb	Isoxathion	Pirimiphos methyl	Triazamate
Clethodim	Fenoprop (2.4.5- TP; Silvex)	Ivermectin B1b	Primisulfuron-Methyl	Triazophos

Climbazole	Fenothiocarb	Ivermectin B1a	Prochloraz	Tribenuron-methyl
Clodinafop-Propargyl	Fenoxaprop-P-Ethyl	Kresoxim-methyl	Procymidon 1TS	Tricyclazol
Clofentezin	Fenpiclonil	Lenacil	Promecarb	Trietazin
Clomazone	Fenpropathrin	Linuron	Prometryn	Trifloxystrobin
Cloquintocet-mexyl	Fenpropidin	Lufenuron	Propachlor	Triflumizol
Coumaphos	Fenpyrazamine	Malaoxon	Propanil	Trimethacarb
Cyanazine	Fenpyroximat	Malathion	Propaphos	Triticonazole
Cyazofamid	Fensulfothion	Mandipropamid	Propaquizafop	Uniconazole-P
Cycloate	Fensulfothion sulfone	MCPA	Propargite	Vamidothion
Cycloxydim	Fenthion oxon	Mecarbam	Propazine	XMC
Cycluron	Fenthion oxon sulfone	Mefenacet	Propetamophos	Zoxamide

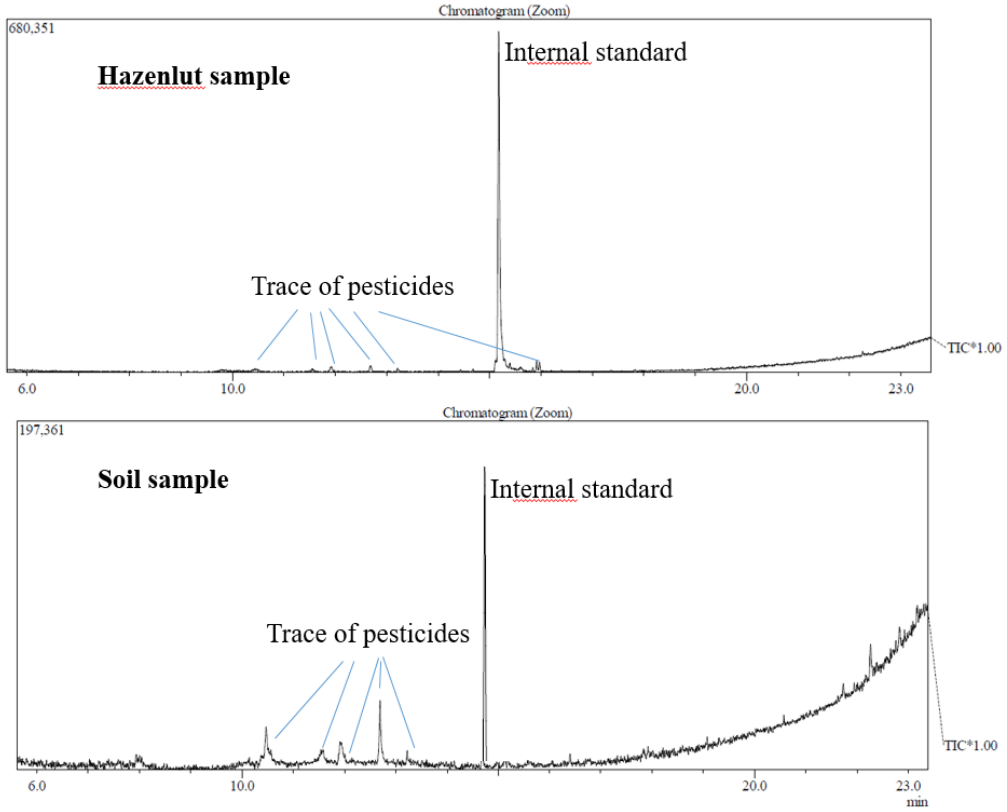

Figure 2. GC/MS/MS analyses of pesticides in hazelnuts and soil samples from Mallakastra, Albania

Figure 2 shown GC/MS/MS chromatograms for hazelnut and soil samples from Mallakastra area. All analyses of hazelnut fruits from Mallakastra area shown that pesticides were not detected (N.D) or their levels were lower than the limit of defect (LOD < 10 ug/kg) in all analysed samples. For hazelnut samples were identified traces of some pesticides such as d-HCH (LOD < 10 ug/kg), Heptachlor (LOD < 10 ug/kg), Heptachlor epoxide (LOD < 10 ug/kg), Aldin (LOD < 10 ug/kg), Dieldrin (LOD < 10 ug/kg), Pyretin (LOD < 10 ug/kg) and Endosulfan I (LOD < 10 ug/kg). Note, that, their levels were always below than allowed level for each of them based on Codex Alimentarius and Albanian norm. Almost the same pesticides were found in soil samples, in a quantity of higher than in hazelnut fruits such as Heptachlor epoxide (22 ug/kg) and Dieldrin (12 ug/kg). Their presence could be because of previous use of pesticides for agricultural purposes in this area. Note that, pesticides found in soil samples could be there because of their previous use of them for other plants/vegetables/cereals not because of their use for hazelnut plants. In addition, it was a fact that generally were found organochlorine pesticides that were regularly used until the 90s in the Myzeqe Field for the treatment of many agricultural crops/fruits/vegetables that grew in this area. Due to their stability, they continue to be reported even today in many studies (Nuro *et al*, 2007; Hvezdova *et al,* 2018; Silva *et al*, 2019). Fortunately, their levels are constantly decreasing due to degradation processes and also the fruits have negligible levels (much lower than the allowed norm for each individual). The way from the soil to the fruits could be a possible source of them but because even in the soil their presence is low then their

levels in the fruits are even lower. Another source of pesticides could be their transport from irrigation water or other atmospheric factors such as rain. Presence of pesticides even in trace level should encourage the responsible institutions for the monitoring of products and soil samples from agricultural areas where pesticides have been used regularly/massively for a long time.

Conclusions

In this study, analyse of pesticide in hazelnut fruits and soil samples from Mallakastra region were performed by using GC/MS/MS and LC/MS/MS techniques. Treatment steps for both samples type was based on the EN ISO 15662:2018 method for foods of plants origin. The method allows determination of more than 600 pesticides and pesticide residues in only run. The procedure is a modular QUEChERS-method recommended by SANTE for the analysis of pesticides in fruits with low water percentage but it is also could be used for soil samples because extraction and clean-up steps are favourable for analyses of pesticides in these samples. Fortunately, it was not observed pesticide levels above the LOD (< 10 mg/kg) which is also the allowed level in EU and Albanian norm. Also, their limit was lower than ADI (Acceptable Daily Intake) based on Cedex Alimentarius levels. For hazelnut samples were identified traces of HCHs, Heptachlors, Aldrin's and Endosulfane. Almost the same pesticides were found in soil samples but in higher level (maximum level up to 20 ug/kg). All these pesticides were organochlorine type. Their presence could be mostly because of their previous use in the same areas where now are built hazel plantations. Even pesticide levels will not exceed the permitted level for any hazelnut and soil sample, their presence (even in trace levels) should encourage the responsible institutions for continuous analysis of fruits, vegetables, cereals, soil samples from areas when in the past pesticides were used widely and for a long time.

Compliance Ethical responsibilities of Authors*: The author has read, understood, and complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors of JIEAS.*

Funding: *There is no funding this study.*

Conflict of Interest: *The authors declare that they do not have any conflict of interest.*

Change of Authorship: *The author has read, understood, and complied as applicable with the statement on "Ethical responsibilities of Authors" as found in the Instructions for Authors and is aware that with minor exceptions, no changes can be made to authorship once the paper is submitted.*

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