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Optimization and validation of a QuEChERS-based method for the simultaneous environmental monitoring of 218 pesticide residues in clay loam soil

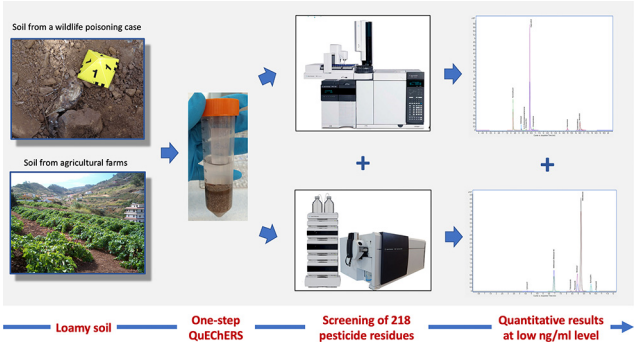
Andrea Acosta-Dacal [a,1], Cristian Rial-Berriel [a,1], Ricardo Díaz-Díaz [b], María del Mar Bernal-Suárez [b], Octavio P. Luzardo [a,*]

[a] Toxicology Unit, Research Institute of Biomedical and Health Sciences (IUIBS), Universidad de Las Palmas de Gran Canaria, Paseo Blas Cabrera s/n, 35016 Las Palmas de Gran Canaria, Spain
[b] Department of Environmental Analysis, Technological Institute of the Canary Islands, C/Los Cactus no 68 35118, Polígono Industrial de Arinaga, Agüimes, Las Palmas, Canary Islands, Spain

HIGHLIGHTS

- Easy method for the sensitive quantification of 218 pesticides in clay loam soils
- One-step QuEChERS-based method without clean-up
- Tested in 18 agricultural soils in which 39 different residues were detected.
- Additional tested in soil samples from a wildlife poisoning incident

GRAPHICAL ABSTRACT



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ABSTRACT

A modified QuEChERS method was optimized, validated and verified for the extraction of 218 pesticide residues in agricultural soil samples. The 218 analytes are extracted using a single step, without clean-up, with matrix-matched calibration, and two complementary techniques: liquid and gas chromatography tandem triple quad mass spectrometry (LC-MS/MS and GC-MS/MS). Some of the parameters such as salts, acidity of the extraction solvent, sample moisture and some mechanical changes in the procedure were optimized to improve the overall performance for the target compounds and the soil matrix. The method was fully validated on a representative agricultural soil sample of the Canary Islands (clay loam soil) in terms of linearity, accuracy and precision. To avoid matrix effects, matrix-matched calibration curves ($R^2 \geq 0.99$) were used for all target analytes. 100% of the compounds can be quantified with limits of quantification (LOQ) lower than the limit typically used in soils (50 ng g^{-1}), with 92% of compounds presenting a LOQ that is at least 10 times lower than that normally required. The limits of detection (LOD) ranged between 0.024 and 6.25 ng g^{-1}. The validated method was applied to a series of actual samples of agricultural soil ($n = 18$). In addition, as a further verification of its potential, the results of the application of the method in the investigation of clay loam soil samples that were obtained from underneath wildlife carcasses in the context of an environmental forensic investigation are also presented.

* Corresponding author at: Toxicology Unit, Clinical Sciences Department, Universidad de Las Palmas de Gran Canaria, Paseo Blas Cabrera Felipe s/n, 35016 Las Palmas, Spain.
E-mail address: octavio.perez@ulpgc.es (O.P. Luzardo).
[1]These authors contributed equally to the work, and therefore should be considered indistinctly as first authors.

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1. Introduction

The current use of pesticides in agriculture exceeds 350,000 tons per year. Their use is so common that the type of agriculture that uses them is called conventional agriculture, as opposed to other "alternative" that does not employ them. The continuous use of pesticides undoubtedly introduces unintended negative environmental impacts, such as the contamination of water sources and soils (Wang et al., 2019). When these agrochemicals are applied to the crop they usually end up in the soil from aerial and ground application (Kumari et al., 2008), where they can be retained by soil materials, be biologically or chemically degraded or be transported to other environmental compartments (Silva et al., 2019). Soil contamination by pesticides may affect soil functions, soil biodiversity, and the food security of subsequent crops (Wang et al., 2019). The high soil persistence of some pesticides is one of the most significant problems faced by farmers when moving to organic farming (Fenoll et al., 2009). However, there is no European regulation that obliges to monitoring programmes at the supranational level, and therefore there is no harmonised analytical methodology and no official list of residues to be monitored in soil. Probably for this reason, there is not clear overview of the level of contamination of agricultural soils at the international level. Most of the available studies focus on the monitoring of a discrete number of permitted (Han et al., 2017; Karasali et al., 2016; Kosubova et al., 2020; Suszter and Ambrus, 2017; Vasickova et al., 2019), or prohibited pesticides (Barron et al., 2017; Eudoxie et al., 2019; Hwang et al., 2018; Kosubova et al., 2020). One of the most recent and complete studies found that 83% of the samples were contaminated with one or more pesticides (Silva et al., 2019). In the case of Spain, a multiannual programme for official control of agricultural production (2016–2020) is currently in force, which focuses mainly on research on pesticide residues in plants, but it also includes soil and water analysis. However, the programme does not refer to the methodology to be used in the analysis of soil samples.

Given the above, there is an increasing need for validated methods capable of quantifying pesticide residues in soil, similar to those used for the mandatory determination of pesticide residues in vegetables (EC, 2019a) or in water (EC, 2000). The extraction procedure employed has to be capable of extracting both the bound and the non-bound residues, with minimal co-extraction of the matrix constituents (Otalvaro and Brigante, 2018).

Pesticide extraction in soils has been carried out using many different extraction techniques: liquid-solid extraction (LSE) (Djurovic et al., 2012), ultrasonic solvent extraction (Castro et al., 2001; Tor et al., 2006), Soxhlet extraction (Wong et al., 2010; Zhou et al., 2013), microwaved-assisted extraction (de Andrea et al., 2001; Merdassa et al., 2013), pressurized liquid extraction (Masia et al., 2015; Vidal et al., 2010), supercritical fluid extraction (Forero-Mendieta et al., 2012; Snyder et al., 1994), solid-phase microextraction (Djurovic et al., 2010; Fernandez-Alvarez et al., 2008), and most recently, modified QuEChERS (Asensio-Ramos et al., 2010; Lesueur et al., 2008), which seems to be one of the most convenient due to the high extraction yields that can be achieved. (Perestrelo et al., 2019). Subsequent analyses have been mostly performed by gas chromatography (GC) (Pastor-Belda et al., 2015; Redondo et al., 1996; Salemi et al., 2013; Zhao et al., 2018), and liquid chromatography (LC) usually tandem coupled to mass spectrometry (LC–MS/MS) (Silva et al., 2019; Zhang et al., 2011).

The aim of this work was to optimize and validate a modified QuEChERS-based extraction method for the quantitative determination of multiple pesticide residues in clay loam soils, to include as many pesticides currently investigated in food products in the EU as possible, but also other environmentally relevant pesticides. The validated method allows the accurate quantification of 218 pesticides and metabolites by means of two complementary analyses by LC-MS/MS and GC–MS/MS. The method was fully applied to a series of actual samples of agricultural soil. In addition, the results of its application to a clay loam soil sample obtained from underneath wildlife carcasses in the context of an environmental forensic investigation are presented.

2. Materials and methods

2.1. Reagents and chemicals

Standard stock solutions of the pesticides subjected to official control in agricultural commodities (EC, 2019a) were purchased from CPA Chem (Stara Zagora, Bulgaria) in 10 compatible mixes (10 μg mL^{-1} each). The rest of the pesticides and the isotopically labeled Procedural Internal Standards (P-IS) were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and Sigma-Aldrich (Büchs, Switzerland), all with a purity superior to 97.1%.

LC-MS grade formic acid (FA, HCOOH), acetic acid (AA, CH_3COOH), acetonitrile (ACN) and methanol (MeOH) were purchased from Honeywell (Morristown, NJ). Ultrapure water was produced in the laboratory using a Gradient A10 Milli-Q System (Millipore, Bedfore, MA, USA). AOAC and EN method QuEChERS salts, and Agilent d-SPE Enhanced Matrix Removal-Lipid (EMR-lipid) were acquired from Agilent Technologies (Palo Alto, USA). Ammonium acetate ($NH_4CH_3CO_2$) and ammonium formate (NH_4CO_2) were obtained from Fisher Scientific (Loughborough, UK).

2.2. Standard stock solutions and mixes

For those pesticides not included in the multiannual coordinated programme (EC, 2019a; Ruiz-Suarez et al., 2015) individual standard stock solutions at a concentration of 1000 μg mL^{-1} were prepared. Intermediate solutions (1 μg mL^{-1}) were used to optimize the mass spectrometer conditions. A working solution containing all the analytes at a final concentration of 0.833 μg mL^{-1}/each was prepared. Additionally, A P-IS mix was prepared at a concentration of 1 μg mL^{-1} in acetonitrile. Matrix-matched calibration curves were prepared with the standard working mix solution, either in soil matrix extracted following the recommended procedure for GC–MS/MS or in a mixture of this extract and ultrapure water (1:1, *v*/v) for LC-MS/MS. All 218 compounds and P-ISs finally included are listed in Table 1. Working solutions were checked periodically for stability.

2.3. Sample selection and pre-treatment

For the method development we chose soil samples from two farms dedicated to organic production. On the basis of its physicochemical properties, this composite can be classified as clay loam soil: pH 4.88, electrical conductivity 209 μS cm^{-1}, oxidizable organic carbon 2.19% (which is equivalent to approx. 3.9% organic matter), 6% moisture and particle size distribution: 29.5% clay, 28.3% fine silt, 11.3% thick slit, 11.5% coarse sand, and 19.4% fine sand.

Additionally, to verify the applicability of the method after the validation process, the method was applied to a series of 18 clay loam agricultural soil samples from the Canary Islands, Spain). In each sampling plot, a composite sample was prepared from at least four subsamples collected at depths between 20 and 30 cm. Then, the soil was homogenized, air-dried at room temperature and sieved (2 mm mesh). Additionally, two clay loam soil samples from a site where animal remains were found in the context of a malicious wildlife poisoning episode were also analyzed.

For the classification of soil samples, electrical conductivity and pH were measured with suitable electrodes in soil-water suspensions (1:5, *w*/*v*). Moisture was calculated as the difference between the air-dried soil weight and the weight after 24 h in an oven at 105 °C. Particle distribution was obtained with the hydrometer method (Ashworth et al., 2001). The oxidizable organic carbon to calculate the organic matter content was determined according to the spectrophotometric method in which the absorbance reading is

Table 1
Compounds analyzed in soil with the category of use, legal status, analysis technique and mass spectrometric conditions.

N°	Compound	Category [a]	Legal status in the EU [b]	Subjected to MRL [c]	Technique [d]	Retention time (min)	LOQ ng g^{-1}	Polarity	Quantification		Confirmation		Fragmentor
									MRM transition (*m/z*)	CE (eV)	MRM transition (m/z)	CE (eV)	
1	4.4′-Dichlorobenzophenone (metabolite of dicofol)	Met	–	No	GC	9.97	0.5	Positive	250.0 → 139.0	15	250.0 → 215.0	5	70
2	4.4′-Dicofol	POP	Not approved	Yes	GC	13.14	20.0	Positive	251.0 → 111.0	15	251.0 → 139.0	45	70
3	Abamectine	I, A, AH	Approved	Yes	LC	10.93	20.0	Positive	890.5 → 567.1	50	895.5 → 751.4	45	160
4	Acephate	I	Not approved	Yes	LC	1.90	0.5	Positive	184.0 → 143.0	0	184.0 → 95.0	20	70
5	Acetamiprid	I	Approved	Yes	LC	4.39	1.0	Positive	223.1 → 126.0	45	223.1 → 90.0	27	140
6	Acrinathrin	I, A	Approved	Yes	LC	10.65	5.0	Positive	559.0 → 208.0	30	559.0 → 181.0	10	76
7	Aldicarb	I	Not approved	Yes	LC	5.09	0.5	Positive	116.0 → 89.1	4	208.0 → 116.0	0	100
8	Aldicarb sulfone	Met	–	Yes	LC	3.15	1.0	Positive	240.1 → 76.0	13	223.1 → 86.1	13	120
9	Atrazine	H	Not approved	No	LC	6.70	1.0	Positive	216.0 → 68.1	15	216.0 → 103.8	30	130
10	Azinphos methyl	I	Not approved	Yes	LC	7.22	0.5	Positive	318.0 → 132.1	15	318.0 → 261.0	8	90
11	Azoxystrobin	F	Approved	Yes	LC	7.53	0.5	Positive	404.1 → 344.1	8	404.1 → 329.1	32	110
12	Benalaxyl	F	Approved	No	LC	8.90	0.5	Positive	326.2 → 148.0	20	326.2 → 208.0	12	90
13	Bendiocarb	I	Not approved	No	LC	5.84	1.0	Positive	224.1 → 166.9	8	224.1 → 108.9	30	100
14	Bifenthrin	I	Not approved	Yes	GC	13.84	20.0	Positive	181.2 → 165.2	25	181.2 → 115.0	60	70
15	Bitertanol	F	Not approved	Yes	LC	9.17	2.5	Positive	338.2 → 70.0	5	338.2 → 269.2	4	100
16	Boscalid (formely nicobifen)	F	Approved	Yes	GC	16.53	5.0	Positive	342.0 → 140.0	15	342.0 → 112.0	45	70
17	Bromopropylate	A	Not approved	Yes	GC	13,84	20.0	Positive	341,0 → 183,0	15	341,0 → 157,0	45	70
18	Bromuconazole (two isomers)	F	Approved	No	LC	8.09/8.67	2.5	Positive	378.0 → 159.0	35	376.0 → 159.0	32	150
19	Bupirimate	F	Approved	Yes	LC	8.30	0.5	Positive	317.2 → 108.1	28	317.2 → 166.1	18	100
20	Buprofezin	I	Approved	Yes	LC	9.79	0.5	Positive	306.1 → 201.0	12	306.1 → 116.0	12	140
21	Cadusafos (ebufos)	I, AH	Not approved	No	LC	9.33	0.5	Positive	271.1 → 159.0	22	271.1 → 131.0	16	100
22	Carbaryl	I	Not approved	Yes	LC	6.16	0.5	Positive	202.1 → 145.1	4	202.1 → 127.1	28	90
23	Carbofuran	I, AH	Not approved	Yes	LC	5.88	0.5	Positive	222.1 → 123.1	20	222.1 → 165.1	30	80
24	Carbofuran-3-hydroxy	Met	–	Yes	LC	4.37	0.5	Positive	238.1 → 163.1	10	238.1 → 181.1	10	110
25	Chlorantraniliprole	I	Approved	Yes	LC	7.27	1.0	Positive	483.9 → 452.9	16	483.9 → 285.9	8	105
26	Chlorfenapyr	I, A	Not approved	Yes	GC	11.97	10.0	Positive	247.0 → 227.0	15	328.0 → 247.0	20	70
27	Chlorfenvinphos	I	Not approved	No	LC	8.98	1.0	Positive	358.9 → 155.1	8	361.1 → 154.9	34	105
28	Chlorobenzilate	A	Not approved	No	GC	12.09	10.0	Positive	251.0 → 139.0	15	251.0 → 111.0	40	70
29	Chlorpropham	H	Not approved	Yes	GC	7.05	0.5	Positive	213.0 → 127.0	15	153.0 → 90.0	10	70
30	Chlorpyrifos	I	Not approved	Yes	GC	9.88	5.0	Positive	314.0 → 258.0	15	314.0 → 286.0	5	70
31	Chlorpyrifos methyl	I	Not approved	Yes	GC	9.07	5.0	Positive	286.0 → 93.0	25	286.0 → 271.0	15	70
32	Chlorthal dimethyl	H	Not approved	No	GC	9.98	2.5	Positive	300.9 → 166.9	55	300.9 → 222.9	25	70
33	Clofentezine	A	Approved	Yes	LC	9.12	2.5	Positive	303.1 → 138.0	12	303.1 → 102.0	40	120
34	Clothianidin	I	Not approved	Yes	LC	4.09	2.5	Positive	250.0 → 169.0	8	250.0 → 131.9	8	100
35	Coumachlor	R	Not approved	No	LC	8.55	0.5	Positive	343.1 → 162.8	15	343.1 → 285.0	15	120
36	Coumaphos	I, A	Not approved	No	LC	8.92	1.0	Positive	363.0 → 227.0	30	363.0 → 306.9	15	120
37	Cyazofamid	F	Approved	Yes	LC	8.42	5.0	Positive	325.0 → 108.0	20	325.0 → 261.1	15	90
38	Cyflufenamid	F	Approved	Yes	LC	9.12	2.5	Positive	413.1 → 223.1	23	413.1 → 295.1	33	70
39	Cyfluthrin (sum of four isomers)	I	Not approved [e]	Yes	GC	16.11/16.2/16.27/16.31	10.0	Positive	226.0 → 206.0	25	226.0 → 199.0	10	70
40	Cyhalothrin (lambda isomer)	I	Approved	Yes	LC	10.43	20.0	Positive	467.0 → 225.0	10	467.0 → 141.0	46	66
41	Cymoxanil	F	Approved	Yes	LC	4.64	0.5	Positive	199.1 → 128.0	4	199.1 → 110.9	12	90
42	Cypermethrin (sum of four isomers)	I	Approved [f]	Yes	GC	16.42/16.51/16.60/16.62	5.0	Positive	163.0 → 127.0	15	163.0 → 109.0	5	70
43	Cyproconazole (two isomers)	F	Approved	Yes	LC	7.97/8.18	0.5	Positive	292.2 → 70.2	18	292.2 → 125.1	24	100
44	Cyprodinil	F	Approved	Yes	GC	10.33	2.5	Positive	224.0 → 118.0	45	224.0 → 104.0	25	70
45	Deltamethrin	I, A	Approved	Yes	GC	18.06	5.0	Positive	181.0 → 152.1	15	251.0 → 172.0	25	70
46	Demeton-*S*-methyl	I, A	Not approved	No	LC	5.92	0.5	Positive	230.9 → 88.9	5	230.9 → 61.0	30	50
47	Demeton-*S*-methyl-sulfone (Dioxydemeton)	I, A	Not approved	No	LC	3.54	0.5	Positive	263.0 → 169.0	24	263.0 → 109.0	12	120
48	Diazinon	I	Not approved	Yes	GC	8.21	0.5	Positive	304.0 → 179.0	15	137.1 → 84.0	20	70
49	Dichlofluanid	F	Not approved	No	GC	9.68	2.5	Positive	224.0 → 123.0	10	226.0 → 123.0	15	70
50	Dichloran	F, MB, WP	Not approved	Yes	GC	7.75	2.5	Positive	206.0 → 176.0	25	206.0 → 148.0	10	70
51	Diethathyl ethyl	H	Not approved	No	LC	8.66	0.5	Positive	312.2 → 238.1	15	312.2 → 162.0	30	120
52	Diethofencarb	F, MB, WP	Approved	Yes	LC	7.52	20.0	Positive	268.2 → 226.1	5	268.2 → 152.0	20	110

(continued on next page)

Table 1 (*continued*)

N°	Compound	Category [a]	Legal status in the EU [b]	Subjected to MRL [c]	Technique [d]	Retention time (min)	LOQ ng g^{-1}	Polarity	Quantification		Confirmation		Fragmentor
									MRM transition (*m/z*)	CE (eV)	MRM transition (m/z)	CE (eV)	
53	Difenoconazole	F, MB, WP	Approved	Yes	LC	9.35	1.0	Positive	406.1 → 250.9	28	406.1 → 337.0	16	176
54	Diflubenzuron	I	Approved	Yes	LC	8.55	1.0	Positive	311.0 → 158.0	32	311.0 → 141.0	8	90
55	Diflufenican	H	Approved	No	LC	9.44	0.5	Positive	395.1 → 266.0	24	395.1 → 246.0	36	150
56	Dimethenamide	H	Approved	No	LC	7.65	0.5	Positive	276.1 → 244.1	10	276.1 → 168.1	20	125
57	Dimethoate	I	Not approved	Yes	LC	4.32	0.5	Positive	230.0 → 198.8	16	230.0 → 125.0	0	70
58	Dimethomorph (two isomers)	F, MB, WP	Approved	Yes	LC	7.68/7.94	1.0	Positive	388.1 → 301.1	20	388.1 → 165.1	32	180
59	Diniconazole-M	F, MB, WP	Not approved	Yes	LC	9.26	1.0	Positive	326.1 → 70.0	28	328.1 → 70.0	28	110
60	Dinocap	F, MB, WP	Not approved	No	LC	10.45	20.0	Negative	295.4 → 193.0	30	295.4 → 163.0	40	150
61	Diphenylamine	PHP	Not approved	Yes	LC	4.24	20.0	Positive	170.0 → 65.0	65	170.0 → 93.0	40	200
62	Endosulfan alfa	POP	–	Yes	GC	11.18	0.5	Positive	241.0 → 206.0	10	195.0 → 160.0	15	70
63	Endosulfan beta	POP	–	Yes	GC	12.19	5.0	Positive	195.0 → 125.0	25	195.0 → 159.0	10	70
64	EPN	I, A	Not approved	No	LC	9.38	10.0	Positive	324.0 → 157.0	25	324.0 → 296.0	14	88
65	Epoxiconazole	F	Approved	Yes	LC	8.40	1.0	Positive	330.0 → 100.9	50	330.0 → 120.9	24	120
66	Esfenvalerate	I	Approved	No	GC	17.54	5.0	Positive	167.0 → 125.1	45	225.0 → 119.0	15	70
67	Ethion (diethion)	I, A	Not approved	Yes	LC	9.95	0.5	Positive	385.0 → 199.0	5	385.0 → 171.0	10	100
68	Ethofumesate	H	Approved	No	GC	9.54	5.0	Positive	286.0 → 207.0	5	286.0 → 161.0	20	70
69	Ethoprophos	I, AH	Not approved	No	LC	8.33	0.5	Positive	243.1 → 97.0	30	243.1 → 130.9	15	90
70	Etofenprox	I, A	Approved	Yes	LC	11.13	1.0	Positive	394.0 → 359.0	10	394.0 → 135.1	40	66
71	Etoxazole	A	Approved	Yes	LC	10.27	0.5	Positive	360.1 → 304.0	28	360.1 → 113.0	26	160
72	Famoxadone	H	Approved	Yes	LC	9.01	2.5	Positive	392.1 → 330.9	5	392.1 → 238.1	12	110
73	Fenamidone	F	Not approved	Yes	LC	7.67	1.0	Positive	312.0 → 92.2	28	312.0 → 236.1	14	100
74	Fenamiphos	I, AH	Approved	Yes	LC	8.57	0.5	Positive	304.1 → 217.1	20	304.1 → 202.0	36	120
75	Fenamiphos sulfone	Met	–	Yes	LC	6.19	0.5	Positive	336.1 → 308.1	23	336.1 → 188.0	31	120
76	Fenamiphos sulfoxide	Met	–	Yes	LC	6.03	1.0	Positive	320.1 → 233.0	20	320.1 → 108.1	44	120
77	Fenarimol	F, MB, WP	Not approved	Yes	GC	15.02	10.0	Positive	139.0 → 75.0	30	139.0 → 111.0	15	70
78	Fenazaquin	A	Approved	Yes	LC	10.65	0.5	Positive	307.2 → 161.1	25	307.2 → 131.0	16	130
79	Fenbuconazole	F, V	Approved	Yes	LC	8.51	2.5	Positive	337.1 → 70.0	40	337.1 → 125.1	33	160
80	Fenbutatin oxide	I, A	Not approved	Yes	LC	11.51	2.5	Positive	519.0 → 90.9	65	519.0 → 197.0	55	180
81	Fenitrothion	I	Not approved	Yes	GC	9.50	10.0	Positive	277.0 → 109.0	15	277.0 → 260.0	5	70
82	Fenoxycarb	I	Approved	Yes	LC	8.63	0.5	Positive	302.1 → 88.0	10	302.1 → 116.1	20	110
83	Fenpropathrin	I, A	Not approved	Yes	LC	10.37	1.0	Positive	367.2 → 125.0	16	350.2 → 125.0	16	72
84	Fenpropimorph	F	Not approved	Yes	LC	7.39	0.5	Positive	304.3 → 147.1	30	304.3 → 130.0	25	120
85	Fenpyroximate	A	Approved	Yes	LC	10.42	0.5	Positive	422.2 → 366.2	12	422.2 → 135.0	36	160
86	Fenthion	I, A	Not approved	Yes	LC	8.82	2.5	Positive	279.0 → 168.8	8	279.0 → 247.1	18	98
87	Fenthion oxon	Met	–	Yes	LC	7.26	0.5	Positive	263.1 → 231.2	16	263.1 → 216.0	24	120
88	Fenthion oxon sulfone	Met	–	Yes	LC	4.61	0.5	Positive	295.0 → 217.0	15	295.0 → 104.2	20	110
89	Fenthion oxon sulfoxide	Met	–	Yes	LC	4.46	0.5	Positive	279.0 → 104.1	20	279.0 → 264.2	28	110
90	Fenthion sulfone	Met	–	Yes	LC	6.32	0.5	Positive	311.0 → 125.0	28	311.0 → 109.0	22	140
91	Fenthion sulfoxide	Met	–	Yes	LC	6.10	0.5	Positive	295.0 → 280.0	15	295.0 → 108.9	30	140
92	Fenvalerate	I	Not approved	Yes	GC	17.34	5.0	Positive	167.0 → 125.1	45	225.0 → 119.0	15	70
93	Fipronil	I, V	Not approved	Yes	LC	8.61	2.5	Negative	435.0 → 330.0	26	435.0 → 249.9	12	116
94	Fipronil sulfide	Met	–	Yes	GC	10.44	5.0	Positive	351.0 → 255.0	20	420.0 → 351.0	35	70
95	Fluazinam	F	Approved	No	LC	9.94	2.5	Negative	462.9 → 416.0	10	462.9 → 398.0	9	140
96	Flubendiamide	I	Approved	Yes	LC	8.75	2.5	Positive	408.0 → 274.0	15	408.0 → 256.0	30	120
97	Flucythrinate (two isomers)	I, A	Not approved	No	GC	16.63/16.82	5.0	Positive	199.1 → 107.1	25	156.9 → 107.1	15	70
98	Fludioxonil	F	Approved	Yes	LC	7.71	5.0	Negative	247.0 → 180.0	62	247.0 → 125.9	32	152
99	Flufenoxuron	I, A	Not approved	Yes	LC	10.30	0.5	Positive	489.1 → 158.0	20	489.1 → 140.9	56	110
100	Fluopyram	F	Approved	Yes	LC	8.18	0.5	Positive	397.0 → 173.0	40	397.0 → 145.0	50	150
101	Fluquinconazole	F	Approved	Yes	LC	8.21	2.5	Positive	376.0 → 307.1	56	376.0 → 108.0	24	140
102	Flusilazole	F, MB, WP	Not approved	Yes	LC	8.59	1.0	Positive	316.1 → 247.1	20	316.1 → 165.0	15	160
103	Flutolanil	F, MB, WP	Approved	No	LC	7.87	0.5	Positive	324.1 → 262.1	16	324.1 → 242.1	24	130
104	Flutriafol	F	Approved	Yes	LC	6.77	1.0	Positive	302.1 → 70.1	16	302.1 → 122.9	28	90
105	Fluvalinate tau	I, A	Approved	Yes	LC	10.81	2.5	Positive	503.0 → 208.0	10	503.0 → 181.0	26	50
106	Fonofos	I	Not approved	No	GC	8.18	0.5	Positive	246.0 → 109.0	5	246.0 → 137.0	15	70

107	Fosthiazate	AH, V	Approved	Yes	LC	6.46	0.5	Positive	284.0 → 104.0	20	284.0 → 227.8	8	110
108	Hexaconazole	F, MB, WP	Not approved	Yes	LC	9.06	2.5	Positive	316.1 → 70.1	20	314.1 → 70.1	20	95
109	Hexaflumuron	I	Not approved	No	LC	9.52	5.0	Negative	459.1 → 439.0	18	459.1 → 276.1	8	100
110	Hexythiazox	A	Approved	Yes	LC	10.10	0.5	Positive	353.1 → 227.9	8	353.1 → 168.1	24	120
111	Imidacloprid	I	Approved	Yes	LC	4.07	2.5	Positive	256.0 → 208.9	12	256.0 → 175.0	12	110
112	Indoxacarb	I	Approved	Yes	LC	9.42	1.0	Positive	528.1 → 293.1	48	528.1 → 202.8	10	140
113	Iprodione	F, MB, WP	Not approved	Yes	GC	13.63	10.0	Positive	314 → 56.0	20	314.0 → 245.0	10	70
114	Iprovalicarb	F	Approved	Yes	LC	8.17	0.5	Positive	321.2 → 119.0	15	321.2 → 202.9	0	108
115	Isocarbophos	I	Not approved	Yes	GC	10.34	5.0	Positive	230.0 → 155.0	25	230.0 → 198.0	10	70
116	Isofenphos methyl	I	Not approved	No	LC	8.75	0.5	Positive	332.1 → 230.9	44	332.1 → 120.9	10	100
117	Isoprothiolane	F, MB, WP	Not approved	Yes	LC	7.87	0.5	Positive	291.1 → 231.1	30	291.1 → 189.0	12	100
118	Kresoxim methyl	F	Approved	Yes	LC	8.74	1.0	Positive	314.1 → 116.0	24	314.1 → 223.0	15	98
119	Linuron	F	Approved	Yes	LC	7.48	1.0	Positive	249.0 → 160.1	20	249.0 → 182.3	8	120
120	Lufenuron	I	Not approved	Yes	LC	10.00	2.5	Negative	509.0 → 339.0	5	509.0 → 326.1	15	90
121	Malaoxon	I	Not approved	No	LC	5.99	0.5	Positive	315.1 → 127.2	12	315.1 → 99.1	12	120
122	Malathion	I	Not approved	Yes	LC	7.87	0.5	Positive	348.0 → 126.7	15	348.0 → 285.0	8	100
123	Mandipropamid	F	Approved	Yes	LC	7.85	0.5	Positive	412.1 → 328.0	8	412.1 → 356.1	4	130
124	Mefenoxam (metalaxyl-M)	F	Approved	Yes	LC	6.90	0.5	Positive	280.0 → 220.0	10	280.0 → 192.0	15	110
125	Mepanipyrim	F, MB, WP	Approved	Yes	LC	8.14	1.0	Positive	224.1 → 106.0	30	224.1 → 77.0	25	120
126	Metaflumizone	I	Approved	No	LC	9.87	0.5	Negative	505.0 → 302.0	10	541.0 → 302.0	20	110
127	Metalaxyl	F	Approved	Yes	GC	9.25	0.5	Positive	234.0 → 146.0	20	249.0 → 146.0	5	70
128	Metaldehyde	M	Approved	No	LC	3.89	20.0	Positive	194.1 → 61.9	5	194.1 → 106.0	5	50
129	Metconazole	F	Approved	No	LC	9.11	0.5	Positive	320.1 → 70.1	33	322.1 → 70.1	24	110
130	Methamidophos	I, A	Not approved	Yes	LC	1.26	0.5	Positive	142.0 → 94.0	12	142.0 → 125.0	12	85
131	Methidathion	I, A	Not approved	Yes	LC	7.05	0.5	Positive	320.1 → 144.8	8	320.1 → 85.0	30	82
132	Methiocarb	I, A, M	Not approved	Yes	LC	7.62	0.5	Positive	226.1 → 169.0	12	226.1 → 121.1	4	90
133	Methiocarb sulfone	Met	–	Yes	LC	4.56	1.0	Positive	258.1 → 122.1	22	258.1 → 201.1	8	100
134	Methiocarb sulfoxide	Met	–	Yes	LC	4.24	0.5	Positive	242.0 → 122.0	28	242.0 → 185.0	22	90
135	Methomyl	I, A, AH	Nor approved	Yes	LC	3.44	1.0	Positive	163.1 → 88.0	8	163.1 → 106.0	5	80
136	Methomyl oxime	Met	–	Yes	LC	2.43	20.0	Positive	106.2 → 58.1	10	106.2 → 42.2	40	70
137	Methoxyfenozide	I	Approved	Yes	LC	7.94	0.5	Positive	369.2 → 149.0	10	369.2 → 313.1	0	80
138	Metrafenone	F	Approved	Yes	LC	9.20	2.5	Positive	409.1 → 209.1	8	411.2 → 209.1	12	120
139	Mevinphos (phosdrin) (two isomers)	I, A	Not approved	No	LC	4.35/4.85	0.5	Positive	225.0 → 193.1	0	225.0 → 127.0	12	65
140	Monocrotophos	I	Not approved	Yes	LC	3.69	0.5	Positive	224.1 → 126.8	15	224.1 → 98.1	12	100
141	Myclobutanil	F, MB, WP	Approved	Yes	LC	8.05	2.5	Positive	289.1 → 70.1	16	289.1 → 125.1	32	110
142	N·*N*-Dimethyl-N′-p-tolylsulphamide (DMST, metabolite of tolylfluanid)	Met	–	No	LC	6.01	0.5	Positive	215.1 → 106.1	4	215.1 → 151.1	10	90
143	N·*N*-dimethylformamidine (DMF, metabolite of amitraz)	Met [g]	–	No	LC	5.40	20.0	Positive	149.9 → 105.8	30	149.9 → 122.9	15	100
144	Nuarimol	F, MB, WP	Approved	No	LC	7.57	2.5	Positive	315.0 → 252.0	30	315.0 → 81.1	28	80
145	Ofurace	F, MB, WP	Approved	No	LC	5.94	0.5	Positive	282.0 → 159.9	20	282.0 → 147.9	30	100
146	Omethoate	I, A	Not approved	Yes	LC	2.56	0.5	Positive	214.1 → 124.8	22	214.1 → 183.0	5	84
147	Oxadixyl	F, MB, WP	Not approved	Yes	LC	5.41	0.5	Positive	279.1 → 219.2	5	279.1 → 132.3	32	110
148	Oxamyl	I, A, AH	Approved	Yes	LC	3.24	0.5	Positive	237.1 → 72.0	12	237.1 → 90.0	5	70
149	Oxamyl oxime	Met	–	Yes	LC	2.76	0.5	Positive	163.3 → 72.1	15	163.3 → 90.0	10	70
150	Oxyfluorfen	H	Approved	No	GC	11.64	5.0	Positive	252.0 → 146.0	20	252.0 → 196.0	40	70
151	Paclobutrazol	H	Approved	Yes	LC	7.86	1.0	Positive	294.1 → 70.1	16	294.1 → 125.2	36	115
152	Paraoxon methyl	I	Not approved	No	GC	8.94	5.0	Positive	230.0 → 106.0	20	230.0 → 136.0	5	70
153	Parathion ethyl	I	Not approved	No	GC	9.90	5.0	Positive	290.9 → 109.0	30	138.9 → 109.0	5	70
154	Parathion methyl	I	Not approved	Yes	GC	9.09	5.0	Positive	263.0 → 109.0	15	263.0 → 79.0	30	70
155	Penconazole	F, MB, WP	Approved	Yes	LC	8.80	0.5	Positive	284.1 → 70.1	30	284.1 → 159.0	15	70
156	Pencycuron	F, MB, WP	Approved	Yes	LC	9.26	0.5	Positive	329.1 → 125.1	24	329.1 → 217.9	12	160
157	Pendimethalin	H	Approved	Yes	LC	10.13	2.5	Positive	282.2 → 212.2	10	282.2 → 194.1	17	80
158	Permethrin (two isomers)	I, A	Not approved	Yes	GC	15.54/16.67	5.0	Positive	183.1 → 168.1	15	183.1 → 165.1	10	70
159	Phosalone	I, A	Not approved	No	LC	9.13	0.5	Positive	385.1 → 182.0	20	385.1 → 110.9	55	80
160	Phosmet	I, A	Approved	Yes	LC	7.27	0.5	Positive	318.0 → 159.9	16	318.0 → 133.0	40	90
161	Phosmet oxon	Met	–	Yes	LC	5.32	0.5	Positive	302.0 → 160.0	10	302.0 → 77.0	55	60
162	Phthalimide (metabolite folpet)	Met [h]	–	No	GC	5.81	5.0	Positive	104.0 → 50.0	25	147.0 → 76.0	25	70

(continued on next page)

Table 1 (*continued*)

N°	Compound	Category [a]	Legal status in the EU [b]	Subjected to MRL [c]	Technique [d]	Retention time (min)	LOQ ng g^{-1}	Polarity	Quantification		Confirmation		Fragmentor
									MRM transition (*m/z*)	CE (eV)	MRM transition (m/z)	CE (eV)	
163	Pirimicarb	I	Approved	Yes	LC	5.17	0.5	Positive	239.1 → 72.1	20	239.1 → 182.1	12	100
164	Pirimiphos ethyl	I, A	Not approved	No	LC	9.86	0.5	Positive	334.1 → 182.1	23	334.1 → 198.1	25	100
165	Pirimiphos methyl	I, A	Approved	Yes	LC	9.08	0.5	Positive	306.1 → 108.1	32	306.1 → 164.0	20	100
166	Prochloraz	F, MB, WP	Approved	No	LC	9.03	0.5	Positive	376.0 → 308.0	10	376.0 → 70.1	20	100
167	Procymidone	F, MB, WP	Not approved	Yes	GC	10.77	5.0	Positive	283.0 → 67.0	40	283.0 → 68.0	25	70
168	Profenofos	I, A	Not approved	Yes	LC	9.67	0.5	Positive	375.0 → 304.8	20	373.0 → 302.8	20	100
169	Propargite	A	Not approved	Yes	LC	10.29	0.5	Positive	368.2 → 231.1	4	368.2 → 175.0	12	88
170	Propiconazole	A	Not approved	Yes	LC	8.96	2.5	Positive	342.0 → 69.0	21	342.0 → 159.0	39	90
171	Propoxur	I	Not approved	No	LC	5.81	0.5	Positive	210.1 → 111.0	12	210.1 → 168.1	0	70
172	Propyzamide (pronamide)	H	Approved	Yes	LC	7.86	1.0	Positive	256.1 → 190.0	16	256.1 → 173.0	25	90
173	Proquinazid	F	Approved	Yes	LC	10.53	1.0	Positive	372.9 → 331.0	20	372.9 → 289.0	5	100
174	Prothioconazole-desthio	Met	–	No	LC	8.44	1.0	Positive	312.0 → 70.1	22	312.0 → 125.0	18	100
175	Prothiophos	F	Not approved	No	GC	11.43	5.0	Positive	162.0 → 63.1	5	266.9 → 221.0	20	70
176	Pyraclostrobin	F	Approved	Yes	LC	9.07	0.5	Positive	388.1 → 193.8	8	388.1 → 163.1	28	120
177	Pyrazophos	F, MB, WP	Not approved	No	LC	9.15	1.0	Positive	374.1 → 222.1	23	374.1 → 194.0	32	100
178	Pyridaben	I, A	Approved	Yes	LC	10.68	0.5	Positive	365.2 → 309.0	8	309.1 → 147.0	16	96
179	Pyridaphenthion	I, A	Not approved	No	LC	8.06	1.0	Positive	341.0 → 189.0	22	341.0 → 92.0	34	100
180	Pyrimethanil	F	Approved	Yes	GC	8.22	0.5	Positive	198.0 → 118.0	40	198.0 → 158.0	20	70
181	Pyriproxifen	I	Approved	Yes	LC	10.01	0.5	Positive	322.2 → 96.0	12	322.2 → 184.9	24	80
182	Quinalphos	I, A	Not approved	No	LC	8.67	1.0	Positive	299.1 → 96.9	20	299.1 → 147.1	30	130
183	Quinoxyfen	F	Not approved	Yes	LC	10.05	0.5	Positive	308.0 → 197.0	32	308.0 → 161.8	55	100
184	Rotenone	I, R	Not approved	No	LC	8.58	1.0	Positive	395.1 → 192.1	25	395.1 → 213.1	20	150
185	Simazine	I	Not approved	No	LC	5.79	0.5	Positive	202.4 → 131.9	20	202.4 → 68.1	30	120
186	Spirodiclofen	A	Approved	Yes	LC	10.44	0.5	Positive	411.1 → 71.2	5	411.1 → 313.0	15	110
187	Spiromesifen	I	Approved	Yes	LC	10.21	1.0	Positive	371.0 → 273.0	25	273.0 → 187.0	15	90
188	Spirotetramat	I	Approved	No	LC	8.26	1.0	Positive	374.2 → 302.2	12	374.2 → 216.1	36	150
189	Spirotetramat-enol	Met	–	No	LC	8.27	5.0	Positive	302.0 → 216.0	20	302.0 → 270.0	30	180
190	Spiroxamine (two isomers)	F	Approved	Yes	GC	9.02/9.47	2.5	Positive	100.0 → 72.0	5	100.0 → 58.0	10	70
191	Tebuconazole	I, A	Approved	Yes	LC	8.85	2.5	Positive	308.2 → 70.2	22	308.2 → 125.1	53	120
192	Tebufenocide	I	Approved	Yes	LC	8.60	0.5	Positive	353.1 → 132.9	22	353.1 → 297.1	0	98
193	Tebufenpyrad	A	Approved	Yes	LC	9.82	0.5	Positive	334.2 → 117.0	47	334.2 → 145.0	37	180
194	Teflubenzuron	I	Not approved	Yes	GC	5.33	0.5	Positive	197.0 → 135.0	25	197.0 → 142.0	25	70
195	Tefluthrin	I	Approved	Yes	GC	8.34	2.5	Positive	177.0 → 127.0	15	177.0 → 87.0	35	70
196	Telodrin (isobenzan)	I	Not approved	No	GC	10.10	2.5	Positive	310.8 → 274.8	5	310.8 → 240.8	25	70
197	Terbufos	I, AH	Not approved	No	GC	8.09	2.5	Positive	231.0 → 129.0	10	231.0 → 97.0	20	70
198	Terbuthylazine	H	Approved	Yes	LC	7.65	0.5	Positive	230.0 → 174.0	16	230.0 → 96.0	28	100
199	Tetrachlorvinphos	I	Not approved	No	LC	8.67	1.0	Positive	367.0 → 127.0	16	364.9 → 127.0	16	110
200	Tetraconazole	F, H	Approved	Yes	LC	8.36	5.0	Positive	372.0 → 159.0	30	372.0 → 70.1	20	100
201	Tetradifon	A	Not approved	No	GC	14.34	2.5	Positive	158.9 → 111.0	15	229.0 → 201.0	20	70
202	Tetramethrin	I	Not approved	No	GC	13.80	5.0	Positive	164.0 → 77.0	30	164.0 → 107.0	15	70
203	Thiacloprid	I	Approved	No	LC	4.76	0.5	Positive	253.0 → 126.0	40	253.0 → 90.0	16	140
204	Thiamethoxam	I	Not approved	Yes	LC	3.56	1.0	Positive	292.0 → 211.1	8	292.0 → 132.0	22	80
205	Thiodicarb	I	Not approved	Yes	LC	6.45	0.5	Positive	355.1 → 88.1	8	355.1 → 108.1	8	60
206	Tolclofos methyl	F, MB, WP	Approved	Yes	GC	9.15	0.5	Positive	265.0 → 93.0	30	265.0 → 220.0	25	70
207	Tolylfluanid	F	No approved	No	GC	10.56	2.5	Positive	238.0 → 137.0	35	238.0 → 91.0	35	70
208	Triadimefon	F, MB, WP	Not approved	Yes	LC	7.97	0.5	Positive	294.1 → 69.3	20	294.1 → 197.2	15	100
209	Triadimenol	F, MB, WP	Not approved	Yes	LC	8.18	2.5	Positive	296.1 → 70.0	10	298.1 → 70.0	10	80
210	Triazophos (hostathion)	I, A	Not approved	Yes	LC	8.12	0.5	Positive	314.1 → 162.0	19	314.1 → 118.9	35	100
211	Trichlorfon	I, AH, V	Not approved	No	LC	4.29	1.0	Positive	256.9 → 109.0	12	258.9 → 109.0	12	170
212	Trifloxystrobin	F	Approved	Yes	LC	9.44	0.5	Positive	409.1 → 186.0	12	409.1 → 145.0	52	110
213	Triflumizole	F	Approved	No	LC	9.49	0.5	Positive	346.1 → 278.0	15	346.1 → 73.0	4	80
214	Triflumuron	I	Approved	Yes	LC	9.13	0.5	Positive	359.0 → 156.0	32	359.0 → 139.0	8	120
215	Trifluralin	H	Not approved	No	GC	7.17	0.5	Positive	306.0 → 264.0	5	264.0 → 160.0	15	70
216	Triticonazole	F	Approved	No	LC	8.34	2.5	Positive	318.1 → 70.1	33	320.1 → 70.1	16	110

217	Vinclozolin	F, MB, WP	Not approved	Yes	GC	9.04	0.5	Positive	212.0 → 145.0	45	212.0 → 109.0	40	70
218	Zoxamide	F	Approved	No	LC	8.96	0.5	Positive	336.0 → 187.1	25	187.1 → 88.9	40	98
1	Atrazine-d5	IS	–	–	LC	6.66	–	Positive	221.2 → 179.0	15	221.2 → 101.0	30	90
2	Carbendazim-d3	IS	–	–	LC	3.45	–	Positive	195.1 → 160.1	15	195.1 → 131.9	30	100
3	Chlorpyrifos-d10	IS	–	–	GC	9.85	–	Positive	324.0 → 260.0	40	324.0 → 195.0	55	70
4	Cyromazine-d4	IS	–	–	LC	1.58	–	Positive	171.0 → 86.0	15	171.0 → 129.0	15	100
5	Diazinon-d10	IS	–	–	GC	8.21	–	Positive	314.0 → 183.0	15	314.0 → 199.0	5	70
6	Linuron-d3	IS	–	–	LC	7.45	–	Positive	255.1 → 159.8	15	255.1 → 185.0	15	100
7	Pirimicarb-d6	IS	–	–	LC	5.12	–	Positive	245.2 → 78.2	5	245.2 → 185.1	15	70

CE: Collision Energy.

[a] POP – persistent organic pollutant, A – acaricide, MB – microbiocide, AH – anthelminthic, F – fungicide, H – herbicide, I – insecticide, R – plant growth regulator, WP – wood preservative, PHP – post-harvest preservative, M – Molluscicide, Met – metabolite, IS – Internal standard.

[b] The legal status reflecting the EU Pesticide Database was considered (https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.selection&language=EN), which is valid for the entire EU.

[c] Pesticide considered in the coordinated multi-annual plan of the EU for the investigation of residues in food of vegetable or animal origin during the years 2020, 2021 and 2022 (Regulation CE/2019/533).

[d] Gas chromatography (GC) or liquid chromatography (LC), both coupled with tandem triple quadrupole mass spectrometry.

[e] Isomer beta (beta-cyfluthrin) is approved until 31 October 2020.

[f] Isomer beta (beta-cypermethrin) has switch to the "not approved" status since September 2017.

[g] The presence of the acaricide amitraz is evaluated through this metabolite.

[h] The presence of the pesticide folpet is evaluated through this metabolite.

compared with a curve of sucrose solutions with increasing carbon concentration.

2.4. Sample preparation

Into a 50 mL centrifuge tube 10 ± 0.05 *g* of dried and sieved soil plus 10 mL of ACN-2.5% FA were added and shaken vigorously. Next, 6 g of $MgSO_4$ and 1.5 g of CH_3COONa were added, shaken vigorously for 1 min and sonicated for 15 min (ultrasonic bath, 50/60 Hz, 120 W). Samples were then placed in a rotatory shaker for 25 min. After that, they were centrifuged for 10 min at 4200 rpm (3175.16 ×g) in a 5804 R Eppendorf centrifuge (Eppendorf, Hamburg, Germany). An aliquot of supernatant extract was filtered through 0.20 μm Chromafil® PET filters (Macherey-Nagel, Düren, Germany). Finally, the supernatant was directly analyzed in GC–MS/MS or diluted with H_2O (1:1, *v*/v) and analyzed in LC-MS/MS.

The samples for recovery experiments and Quality Controls (QCs) were spiked with the required volume to achieve the desired concentration of the standard mix solutions and were left to stand for 1 h prior to extraction. 100 μL of P-IS mix solution was added to all samples in the same step, including the blanks.

2.5. Instrumental analysis

2.5.1. LC-MS/MS

LC-MSMS analysis of 167 compounds was conducted using a 1290 Infinity II LC System coupled to a Triple Quad 6460 mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). The column was a Poroshell 120 EC-C18 column (2.1 × 100 mm, 2.7 μm; Agilent Technologies) equipped with a guard pre-filter with a 0.3 μm SS frit and a pre-column (2.1 × 5 mm, 1.8 μm; Agilent Technologies) at 50 °C. The mobile phases consisted on 2 mM ammonium acetate 0.1% FA in ultrapure water (A) and 2 mM 0.1% FA ammonium acetate in MEOH (B). A binary gradient using mobile phases A and B was programmed as follows: 5% B - 0.5 min; 5% B - 1 min; 40% B - 2.5 min; 85% B - 8 min; 100% B - 10 to 14 min; 5% B - 14.01 min (total run = 18 min). The flow rate was 0.4 mL min^{-1} and the injection volume was 5 μL.

MS/MS analyses were performed using the Agilent Jet Stream Electrospray Ionization Source (AJS-ESI), in both positive and negative ionization mode, with dynamic multiple reaction monitoring (dMRM). The nitrogen supplied by Zefiro 40 nitrogen generator (F-DGSi, Evry, France) was used as desolvation and drying gas. Nitrogen (99.9999% purity) was used as collision gas. The sheath gas temperature was 330 °C and the flow rate was 12 L min^{-1}. The desolvation and nebulizing gas temperature was 190 °C and the flow rate was 11 L min^{-1} with a pressure of 26 psi. The capillary voltages were set at 3900 and 2600 V in positive and negative ionization mode, respectively. The cycle time was 700 ms and dwell time 3–83 ms.

2.5.2. GC-MS/MS

The GC-MS/MS analysis of 51 compounds was performed with a GC System 7890B equipped with a 7693 Autosampler and Triple Quad 7010 mass spectrometer (Agilent Technologies, Palo Alto, USA). The columns were two fused silica ultra-inert capillary columns Agilent J&WHP-5MS (Crosslinked 5% phenyl-methyl-polysiloxane, Agilent Technologies) 15 m length, 0.25 mm i.d., and 0.25 μm film thickness of 0.25 μm each connected in series by a Purged Ultimate Union (PUU; Agilent Technologies). The use of two 15 m columns instead of one of 30 m permitted the use of the back-flushing technique. Helium (99.999%) was used as the carrier gas and the flow was adjusted by the retention time lock feature using chlorpyrifos methyl as a reference (retention time = 9.143 min). The column temperature was maintained at 80 °C for 1.8 min, increased to 170 °C at a rate of 40 °C min^{-1}, then increased to 310 °C at a rate of 10 °C min^{-1} and held for 3 min. The injection volume was 1.6 μL in splitless mode using a 4 mm Ultra Inert Liner with glass wool (Agilent Technologies) and it was set at 250 °C. Each

chromatographic analysis lasted 20.75 min. Post-run backflush was set at −5.8 mL min^{-1} and 315 °C for 5 min.

MS/MS analyses were performed using electron impact (EI) ionization source in multiple reaction monitoring (MRM) mode. The EI source temperature was set at 280 °C. Nitrogen 6.0 (99,9999% purity, Linde, Dublin, Ireland) was used as the collision gas at a flow of 1.5 mL min^{-1}. The transfer line temperature was 280 °C. A solvent delay of 3.7 min was left. The cycle time was in the range of 52–334 ms and the dwell time was between 15 and 40 ms.

2.6. Method validation parameters

The validation of the developed method was performed following the recommendations of the European Union SANTE 12682/2019 and the SANCO 825/00 Rev.1 guidance document on residue analytical methods (EC, 2010; EC, 2019b), which were followed in the absence of specific guidelines for the analysis of pesticide residues of pesticides in soil. The procedures are detailed in the accompanying Data in Brief article entitled "*Supporting dataset on the optimization of a QuEChERS-based method for the determination of 218 pesticide residues in clay loam soil*".

3. Results and discussion

3.1. Optimization of chromatographic and spectrometric conditions

3.1.1. LC-MS/MS

The optimization of MS/MS conditions for each compound, including the search for the precursor and product ions and the collision energy, was performed injecting directly to the mass spectrometer 5 μL of either individual solutions or discrete mixtures of maximum 15 compounds at 1 μg mL^{-1}/each in ACN. The mobile phases used in this stage were 2 mM ammonium formate 0.1% AA in ultrapure water (A) and in MEOH (B) in isocratic mode (50:50, *v*/v). The precursor ion and the fragmentor were selected using a MS2 scan. The product ions were optimized using product ion scanning at different collision energies, choosing those with the higher response.

Most of the analytes were determined in positive mode except for a few of which gave a better response in negative mode (Table 1). The precursor ions corresponded to $[M + H]^+$ and $[M + H]^-$ in positive and negative mode, respectively, except for some of them (acrinathrin, aldicarb, cyhalothrin (lambda), etofenprox, famoxadone, fenpropathrin, malathion, metaldehyde, methidathion, oxamyl, phosalone and propargite) which formed ammonium adducts $[M + NH4]^+$. For other analytes (abamectin, aldicarb sulfone, dinocap, fenbutatin oxide and flubendiamide), specific ions were used as precursor ions. In some compounds containing elements with a characteristic isotope distribution in their structure, such as Cl and Br in hexaconazole and metrafenone, respectively, transitions corresponding to ^{35}Cl and ^{37}Cl or ^{79}Br and ^{81}Br were selected. The transitions were selected in terms of selectivity and sensitivity, choosing the most abundant for quantification proposes.

After selecting the best combination of MRM transitions for each target analyte and P-IS, chromatographic and source conditions were optimized. These experiments were performed by injecting standards at 20 ng mL^{-1} in ACN (in triplicate). The final conditions selected were then tested with a matrix-matched standard at the same concentration.

The source parameters were optimized using Mass Hunter Source Optimizer software (Agilent Technologies, Palo Alto, USA). These parameters include gas temperature, gas flow, nebulizer gas pressure, sheath gas flow and temperature, capillary voltage and nozzle voltage.

Two reverse phase columns were tested for the chromatographic separation performance: the ZORBAX Eclipse Plus C18 (2.1 mm × 50 mm, 1.8 μm, Agilent Technologies) and the Poroshell 120 EC-C18 column (2.1 × 100 mm, 2.7 μm; Agilent Technologies). The Poroshell column showed a better performance in terms of peak shape and column pressures (under 400 bar while with the ZORBAX column was over 600 bar), which is better for long-term equipment protection. The mobile phase and its gradient were optimized to obtain a good separation of the compounds along the chromatogram. The phase modifiers ammonium acetate, ammonium formate, FA and AA were compared. No major differences were achieved with any of the weak acids and 0.1% FA was selected after choosing it as solvent extraction modifier (see Section 3.2 Optimization of the Extraction Method). On the other hand, better areas and peak shapes were obtained when using 2 mM ammonium acetate in water and organic phase solvent.

To study the injection volume we tested 1, 2, 5, 10 and 20 μL, being 5 μL the final choice due to the good responses obtained. The use of higher volumes resulted in detector saturation. Finally, the dilution of the sample extract was assessed. The selected compounds belong to different chemical groups and, therefore, have a wide range of polarities which could result in poor chromatographic separations. The dilution of the final extract, in ACN-2.5% FA, not only contributed to reduce possible matrix effects, but also produced better peak shapes for compounds such as monocrotophos. The selected sample dilution was water-extract 1:1 (*v*/v) as a compromise between sensitivity, peak shape and selectivity for all compounds.

3.1.2. GC-MS/MS

Our laboratory had an important database of compound transitions for GC–MS/MS which were optimized for the needs of the method. Firstly, all available transitions for the target analytes were tested by injecting a 100 ng mL^{-1} mix standard solution in order to find out the most promising transitions. Due to the complexity of the soil matrix, transitions were selected giving priority to selectivity over sensitivity to avoid possible interference from the matrix components. This was evaluated by comparing 100 ng mL^{-1} of the prepared mix standard solution in the solvent against that of the matrix extract. Once the best transitions were selected, the optimal collision energies were determined by injecting the standard solution in a range of 0–65 V, tested in 5 V increments. The transitions were distributed in 24 MRM windows to achieve good sensitivity, dwells, and cycle time.

As mentioned throughout the text, ACN-2.5% FA extracts were injected directly into the gas chromatographer, although this is not the most common solvent chosen for GC analyses. This decision was taken after noting that some analytes were lost or partially degraded during the evaporation steps required for a solvent change. In addition, ACN has proven to be a suitable solvent for GC injection in other method development papers (Mastovska and Lehotay, 2004). Adequate peak shape and sensitivity were achieved even at low concentrations for all analytes.

The chromatographic parameters had been previously optimized by our group, so no further modifications were made either to the oven temperature ramp or to the column type due to the good results obtained for similar analytes (Luzardo et al., 2015; Luzardo et al., 2014). However, as the solvent chosen in those methods had been cyclohexane, it was necessary to optimize some parameters. The initial oven temperature was set at 80 °C, close to the boiling point of ACN, to avoid condensation in the column. The injector temperature and the injection volume were studied in the range of 230–290 °C and 1–1.6 μL, respectively, taking into account the vapor pressure solvent in the liner. Finally, the temperature of the ionization source and the temperature of the transfer line were studied in increments of 10 °C from 250 to 320 °C and 270–320 °C, respectively.

The precursor and product ions, retention times, fragmentation and collision energies of all the compounds are shown in Table 1. Fig. 1 shows the chromatograms of a blank soil sample spiked at 20 ng g-1with the target analytes and P-IS by the LC-MS/MS and GC–MS/MS analyses.

3.2. Optimization of the extraction method

A QuEChERS-based method for the extraction of target pesticides in the soil was investigated. Some parameters, such as the combination of salts, the acidity of the extraction solvent, moisture of the sample and some mechanical changes in the procedure were studied in order to achieve the best extraction efficiency. To facilitate the optimization, all experiments were done at the same concentration of 20 ng g^{-1} in triplicate.

We decided not to modify the sample quantity used in the original QuEChERS procedure (10 g) as it provides a combination of practicality and representativeness. Similarly, ACN was used as the extraction solvent because of its suitability for a wide range of compound polarities and no higher volume (10 mL) was required as sufficient supernatant volume was collected. Our first approach was to introduce a few modifications in the mechanical aspects of the procedure. A 15-min sonication step from a time-course experiment (up to two hours) was chosen. This step was included just after adding the QuEChERS salts and vigorously shaking the tubes, to produce further decomposition of possible aggregates (Asensio-Ramos et al., 2010). Likewise, 25 min of rotatory shaking were introduced after the sonication step to increase the interface and contact time between the extractant solvent and the soil.

The two main official variants of the original QuEChERS, the AOAC method (Lehotay, 2007) and the EN method (EN, 2019), were compared in order to select the most appropriate for the target pesticides and metabolites and the soil matrix: 1.5 g of NaOAc and 6 g $MgSO_4$, in the AOAC procedure, and 4 g $MgSO_4$, 1 g NaCl, 1 g sodium citrate dihydrate and 0.5 g sodium hydrogen citrate sesquihydrate in the EN method. After centrifugation, the extract was either collected for analytical determination or further purified. The clean-up is intended to reduce matrix components that may remain in the extract after the first extraction step. This step is typically achieved by d-SPE using secondary amine (PSA), C18 and graphitized carbon black (GCB), either alone or in mixtures (Pszczolinska and Michel, 2016). Nevertheless, we have seen that these sorbents usually retain some of the more polar compounds reducing recoveries, which is consistent with what other authors have described (Caldas et al., 2011). Instead, the d-SPE clean-up was approached by the use of Enhance Matrix Removal (EMR), a proprietary lipid removal sorbent patented by Agilent Technologies (Agilent, 2015), that had not been tested in soil samples previously. The mean recoveries obtained in these experiments (AOAC vs. EN QuEChERS extraction, with or without an additional EMR-clean-up step) are graphically presented in Fig. 1 of the accompanying Data in Brief. In general, the recovery percentages and peak shapes for most of the 218 compounds included in this method were better with the AOAC salts. Not surprisingly, the clean-up did not provide any improvement but on the contrary, a large amount of the compounds either reduced their extraction performance or were lost. Therefore, the addition of a clean-up step (either with PSA, C18, GCB, or EMR) was discarded because it hardly improved selectivity and appeared to have minor changes of the matrix effect (Supplementary Figs. 1–3).

The original AOAC method for the analysis of plants uses 1% AA in the extraction solvent to adjust the pH. Nevertheless, we identified the percentage and type of acid employed to acidify the ACN as the next variable to be optimized in adapting this method to the pesticide extraction from clay loam soils. Therefore, in addition to AA, we also tested FA and compared the extraction in the presence of 1% of each acid with that of no acid added. It was noted that acidification definitely improved the recovery for the vast majority of analytes. In addition, we also verified that this improvement was higher with FA instead of with AA. Then, to find out the optimized percentage of FA, it was tested at 0.5%, 1%, and 2.5%. We did not consider the inclusion of higher percentages of acid, since it has been described that extreme pH conditions can affect the stability of many pesticides (i.e. acetamiprid is unstable at pHs below 4 and above 7) (Schilder, 2008). From our results, it can be concluded that the extraction efficiency of most of the chemicals under study improved with the increase of FA in the solvent. Thus, ACN acidified with 2.5% F.A was set as the extraction solvent. The detailed results are shown in Figs. 2 and 3 of the accompanying Data in Brief article.

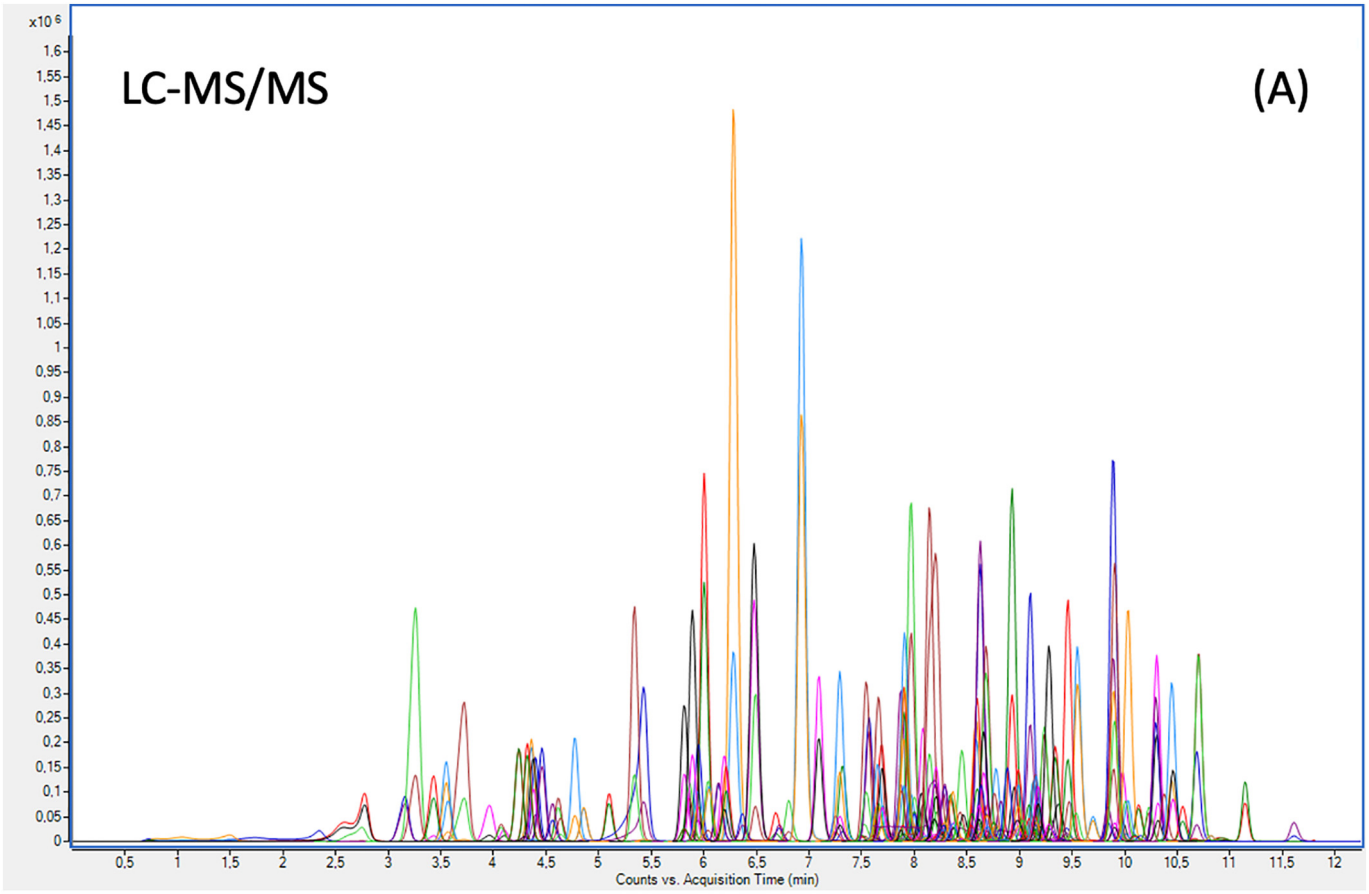
The original QuEChERS method was developed for fruits and vegetables, which are samples with high water content (> 70%). Therefore, when processing dry samples with QuEChERS it is common to add some amount of water (Grande-Martinez et al., 2015), and in fact, in soil samples it has been described that the addition of water could make the pores more accessible to the extraction solvent (Pinto et al., 2010). Thus, adding water to the soil samples was the next step in the optimization process. Deionized water was added to aliquots of the air-dried soil sample to reach 10, 20, 30, 40 and 50% of moisture. The samples were left to hydrate for one hour. We did not observe large differences in the recoveries of the compounds determined in LC/MS-MS technique with the increase of moisture. Nonetheless, as the percentage of moisture increased, the results were worse for many of the compounds analyzed by GC–MS/MS. A possible explanation could be the remaining water in the extract which not only is not a suitable solvent for GC chromatography but also reduced the matrix load in the sample and, therefore, the sensibility. To solve this problem of excess polarity of the injection solvent in the GC–MS/MS (ACN containing a certain percentage of water) it would have been necessary to add an evaporation step of the obtained extract to completely eliminate the water and be able to change the solvent, which had been previously discarded (detailed results in Fig. 4, Data in Brief).

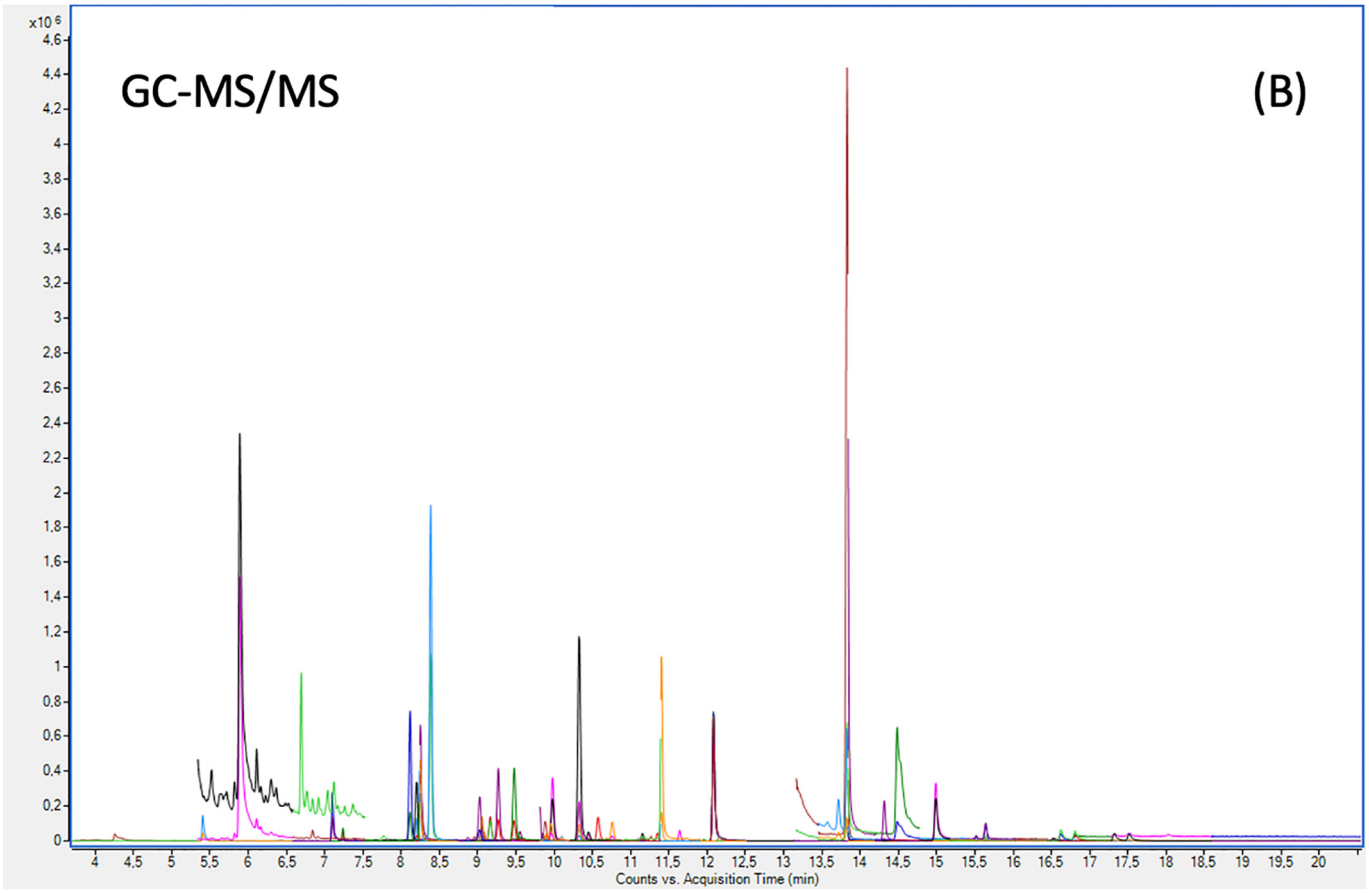
3.3. Method validation

The optimized QuEChERS-based method was validated in terms of linearity, accuracy and precision following the agreements stated in the “Method Validation Parameters” section.

The complexity of the soil matrix may have some effect on the analysis, either by suppressing or enhancing the response, that may compromise the accuracy, selectivity and sensitivity of the method (Asensio-Ramos et al., 2010; Matuszewski et al., 2003). In order to assess these possible interferences in the chromatographic response, a matrix effect study was performed. The calibration curves, either in the matrix extract or in the solvent (both diluted with water (1:1, *v*/v) for LC-MS/MS) were prepared in the range of 6.25–50 ng mL^{-1} in triplicate. The matrix effect (ME) was evaluated comparing the response obtained for each analyte in the soil extract with that given in the solvent at the same concentration in both equipment, extracting the blank to the soil matrix signal. No significant matrix effects were considered when ME was between 80 and 120% (EC, 2010; EC, 2019b). Fifty-four compounds presented significant enhancement caused by the co-extraction of matrix components, fifty of which were compounds analyzed by GC–MS/MS, representing 98% of the total compounds analyzed by this technique. These results have shown the importance of evaluating the matrix effect on this equipment, where the presence of high amounts of matrix components could protect the analyte from adsorption or degradation during evaporation in the inlet (Fernandes et al., 2013). In contrast, the main trend observed for ME in LC-MS/MS was towards signal suppression although this was not significant for most of them (135 compounds) and only 6 presented strong or medium signal suppression. However, to improve the accuracy of the quantification, as well as to simplify the procedure, it was decided to use matrix-matched calibration in both techniques (detailed results in Fig. 5, Data in Brief).

The linearity was obtained from a triplicate range of 9 levels (from 0.39 to 100 ng g^{-1}). The response was satisfactory for all the compounds, with a deviation of back-calculated concentration from true concentration < 20%, for both GC–MS/MS and LC-MS/MS, either in matrix extract or in matrix-extract diluted with water (1:1, v/v), respectively. R^2 values were above 0.99 for all analytes in both techniques (Table 2, Data in Brief).


LC-MS/MS
(A)
x10 6
Counts vs. Acquisition Time (min)


GC-MS/MS
(B)
x10 6
Counts vs. Acquisition Time (min)

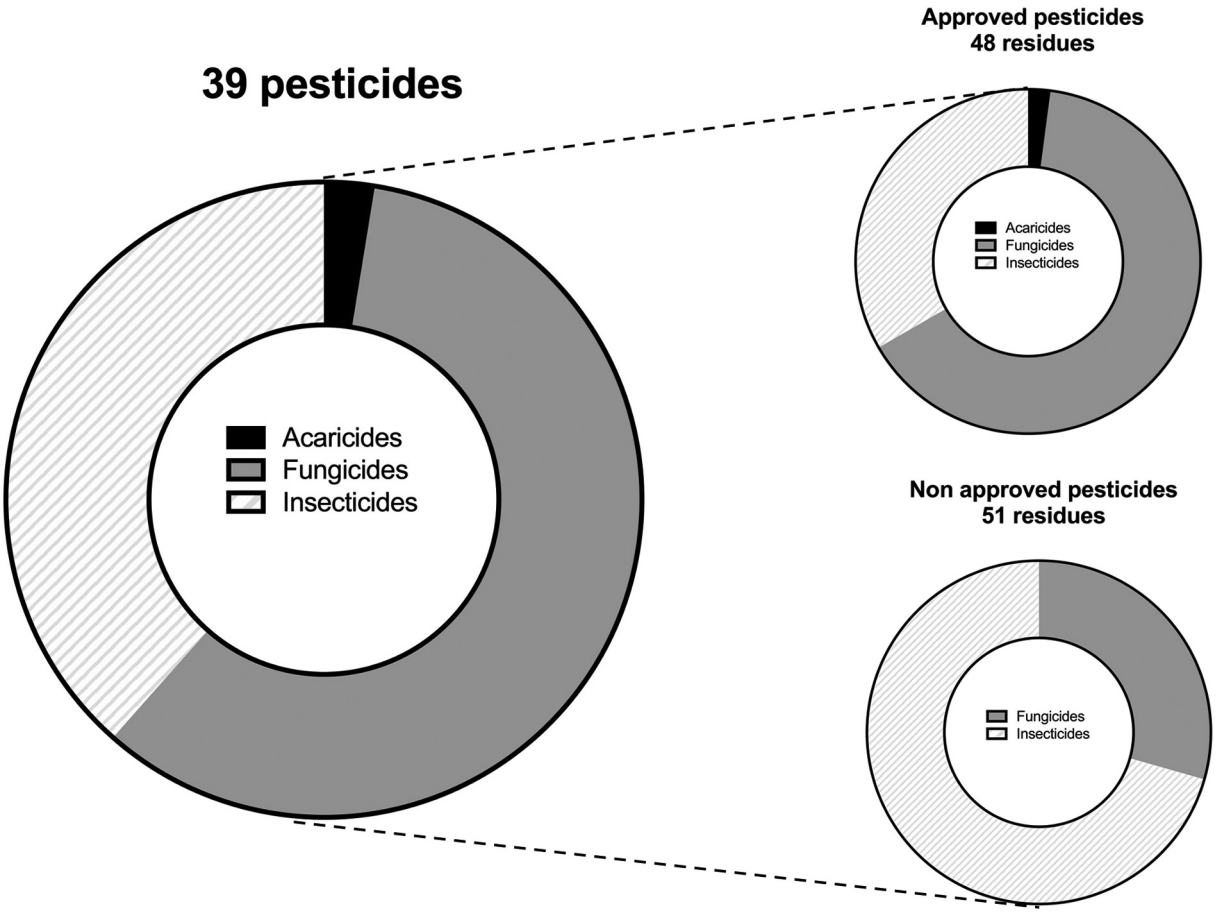


Fig. 2. Distribution of pesticide residues detected in the 18 soil samples, classified by target pest.

The accuracy and the precision of the method were tested with recovery experiments at 7 concentration levels in quintuplicate: 0.5, 1.0, 2.5, 5, 10, 20 and 50 ng g^{-1}. The highest concentration of this range is usually selected as an acceptable LOQ for pesticide residue analyses in soil (EC, 2010; EC, 2019b). The method presented satisfactory accuracy (recoveries in the range 70–120%) and precision (RSD < 20%) for 198 analytes (90.8% of the compounds) for all the fortification levels ranging from the highest concentration (50 ng g^{-1}) to the LOQ set for each analyte. As the LOQ we chose the lowest level of fortification that met all the validation criteria. Although 18 compounds presented recoveries over 120% or below 70% between their LOQ and 50 ng g^{-1}, they were included in the final method due to their importance for pesticide monitoring in soils. In fact, the SANTE guidelines take this situation into account while allow for the validation of compounds in the range of 60–140% if they show high reproducibility (RSD < 20%) in routine analyses, which was the case for these compounds (EC, 2019a). Additionally, two compounds (dichloran and nuarimol) presented recoveries between 70 and 120% at 5 ng g^{-1}, but a high variability (RSD >20%). However, this is also acceptable for concentration levels below 10 ng g^{-1} in pesticide residues in soil, according to the guidelines we have followed (EC, 2010). In total, 90% of the compounds had an LOQ equal to 5 ng g^{-1} or below, which is 10 times lower than the typically fixed value for these residues in soil. On the other hand, the Limits of Detection (LODs) were determined as the lowest point of the calibration curve having a signal-to-noise ratio above 3 (Peak-to-Peak algorithm) and having acceptable accuracy (80–120%). For this purpose, matrix-matched calibration curves in the range of 0.024 to 100 ng g^{-1} were prepared in triplicate and injected in each equipment. Detailed results are presented in Table 2 of the accompanying Data in Brief.

After the validation process, the proposed method proves to be accurate and reliable for the analysis of the pesticides selected in this study in clay loam soil samples.

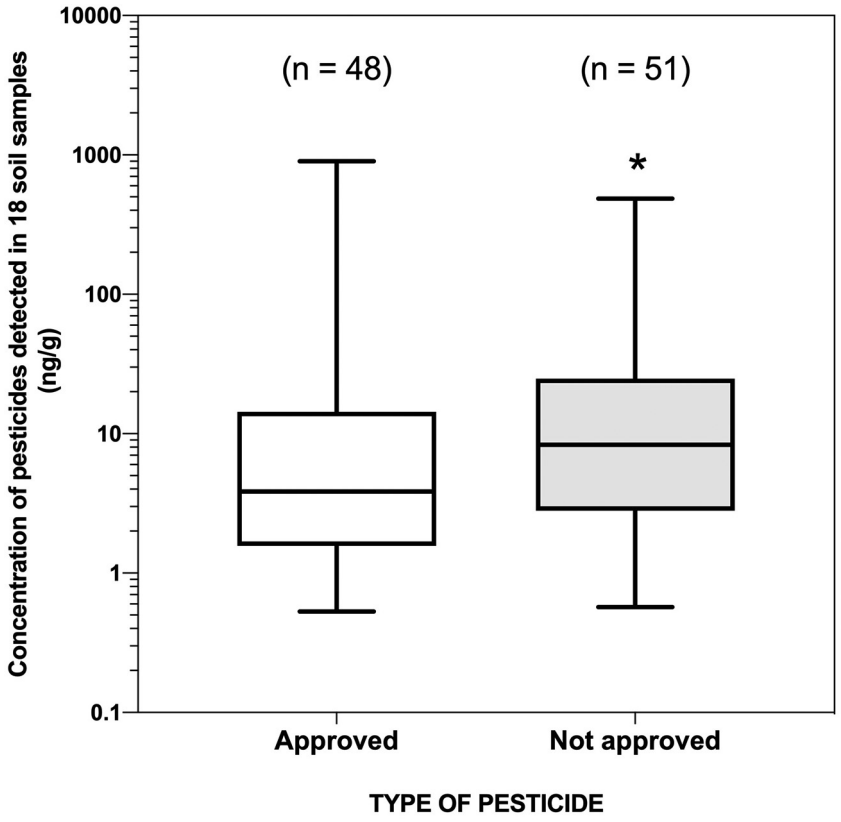
3.4. Application of the method to real samples

The developed method was applied to soil samples from two different scenarios. Firstly, a series of 18 soil samples from farmlands were analyzed, all of them with the characteristics of the soil employed in the method validation. In addition, two soil samples from the investigation on a wildlife poisoning case were also analyzed.

3.4.1. Monitoring of agricultural land

The samples came from 3 farm vineyards, 3 mixed vegetable farms, 3 fruit tree farms, 3 banana farms, 3 farms with crop in transition to organic production, 1 avocado farm, and 2 abandoned farmlands. The summary of the results obtained is shown in Table 2. It should be noted that there were only three samples in which no pesticide residues were detected (one abandoned farm, the avocado farm, and one fruit tree farm). Thus, the detection range was 0 to 18 residues per sample, although most (61%) ranged 2 to 6 residues. A total of 109 residues above LOQ were identified, belonging to 39 different pesticides (and metabolites), which represents 17.9% of the analytes included in the

Fig. 1. Chromatograms of the analyses by LC-MS/MS **(A)** and GC–MS/MS **(B)** of a blank soil sample spiked with the 218 compounds and the P-IS at 20 ng g^{-1}.



Mann Whitney test	
P value	0.0474
Exact or approximate P value?	Exact
P value summary	*
Significantly different (P < 0.05)?	Yes
One- or two-tailed P value?	Two-tailed
Sum of ranks in column A,B	2117 , 2833

Fig. 3. Box and whiskers graph showing the distribution of the detected residue concentrations. We show them separated by authorized (left) and non-authorized (right) active ingredients in the EU. The lines show the medians, the boxes cover the 25th to 75th percentiles, and the minimal and maximal values are shown at the ends of the bars. The *P* value was calculated by the Mann-Whitney *U* test because the series of values did not fit the normal distribution (Kolgomorov-Smirnoff test).

method. Of these, 9 were detected in more than 20% of the soil samples (4,4′ dichlorobenzophenone (DBP), fenbutatin oxide, buprofezin, alpha-endosulfan, fenamiphos sulfoxide, benalaxyl, boscalid, fenarimol and penconazole). Of these frequently detected compounds, most are approved for cultivation in the EU (EC, 2020). It is worth noting the case of DBP, since it is the most frequently detected residue (72% of the samples), although at relatively low concentrations. Although it is identified in Tables 1–2 as "metabolite of dicofol", the truth is that DBP could also originate (in rare cases) from 4, 4′-DDT by fungal degradation (*Xerocomus chrysenteron*), or from chlorobenzilate or other organochlorine compounds. The only exception is soil #9 (Table 2) in which 25 ng g^{-1} of dicofol was also detected. We believe it is possible to state that the insecticide dicofol was applied on this farm in a relatively recent time. However, in all other cases we cannot assure that the residue comes from the application of dicofol.

We noted that EU non-authorized pesticides were higher both in number of residues (Fig. 2) and in concentration (Fig. 3). The most frequently detected class of pesticide among the authorized active substances was fungicides. Some of them are already known to remain strongly retained in the soil such as fenbutatin oxide (Gray et al., 1995), boscalid (He et al., 2020) or benalaxyl (Qin et al., 2014). For others, such as buprofezin (Oulkar et al., 2009) or penconazole (Abd-Alrahman and Ahmed, 2012), a rapid degradation rate (especially in loamy soils) has been described, and its detection would point to a very recent use of these products. In contrast, most of the detected residues of unauthorized active substances belong to the group of insecticides (Fig. 2).

Fig. 3 shows the distribution of the concentrations found, divided also between unauthorized and authorized substances. As can be seen, although the highest residue values found in soil correspond to some authorized substances (such as deltamethrin in soil #11, Table 2), the residue concentration values of the unauthorized active substances are significantly higher than those of residues of the authorized active substances.

From our results it cannot be deduced that there is a type of crop that generates a greater amount of residue in the soil, and the variability is high. However, the small sample size of the study precludes any firm conclusions.

The case of soil #16 called our attention. This sample presented the greatest number of residues ($n = 18$), and comes from a farm vineyard, whose phytosanitary treatment records we know about.

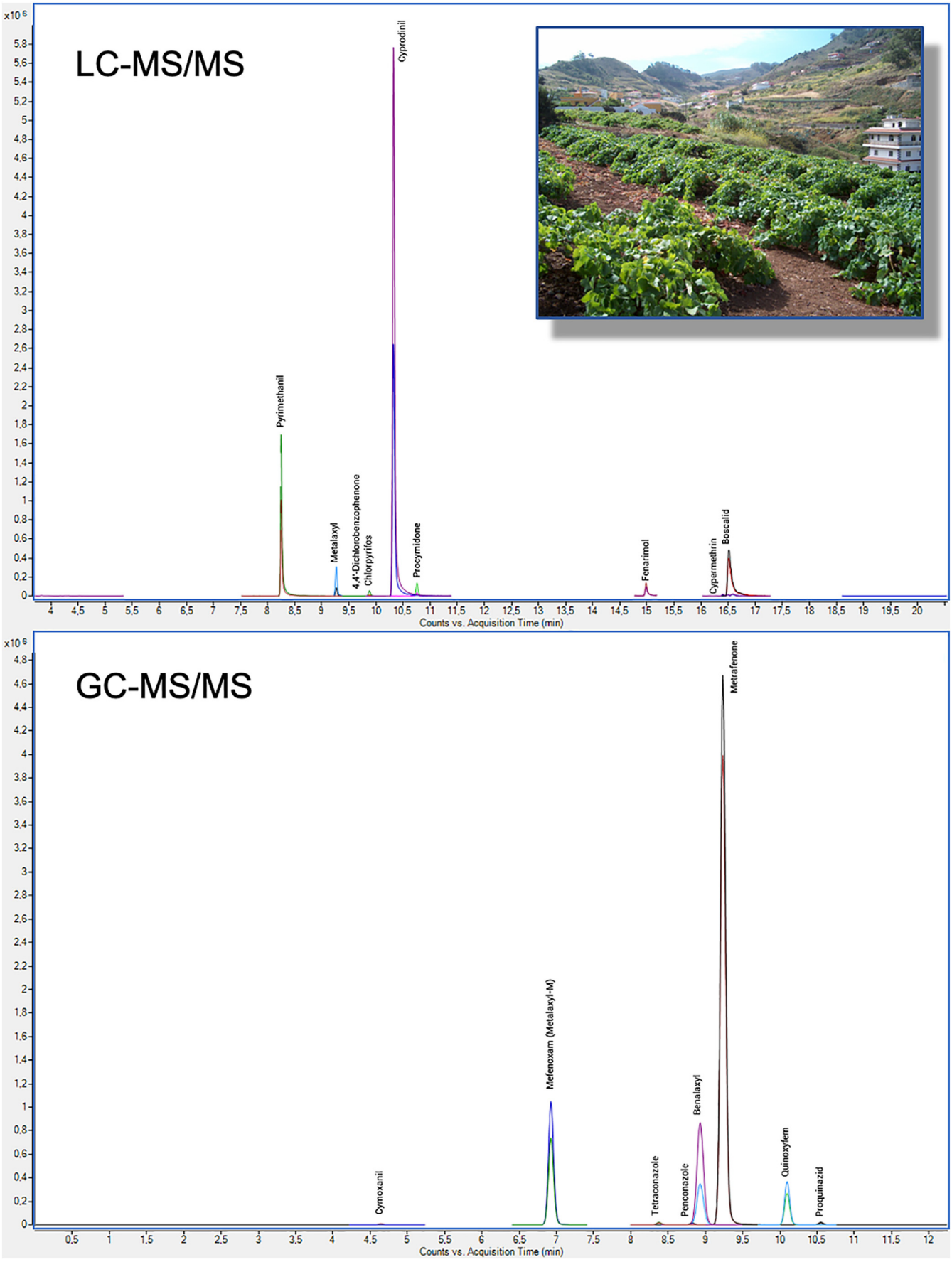


Fig. 4. Chromatograms with the identification of the 18 residues detected in soil sample #16 (small-scale family-run vineyard).

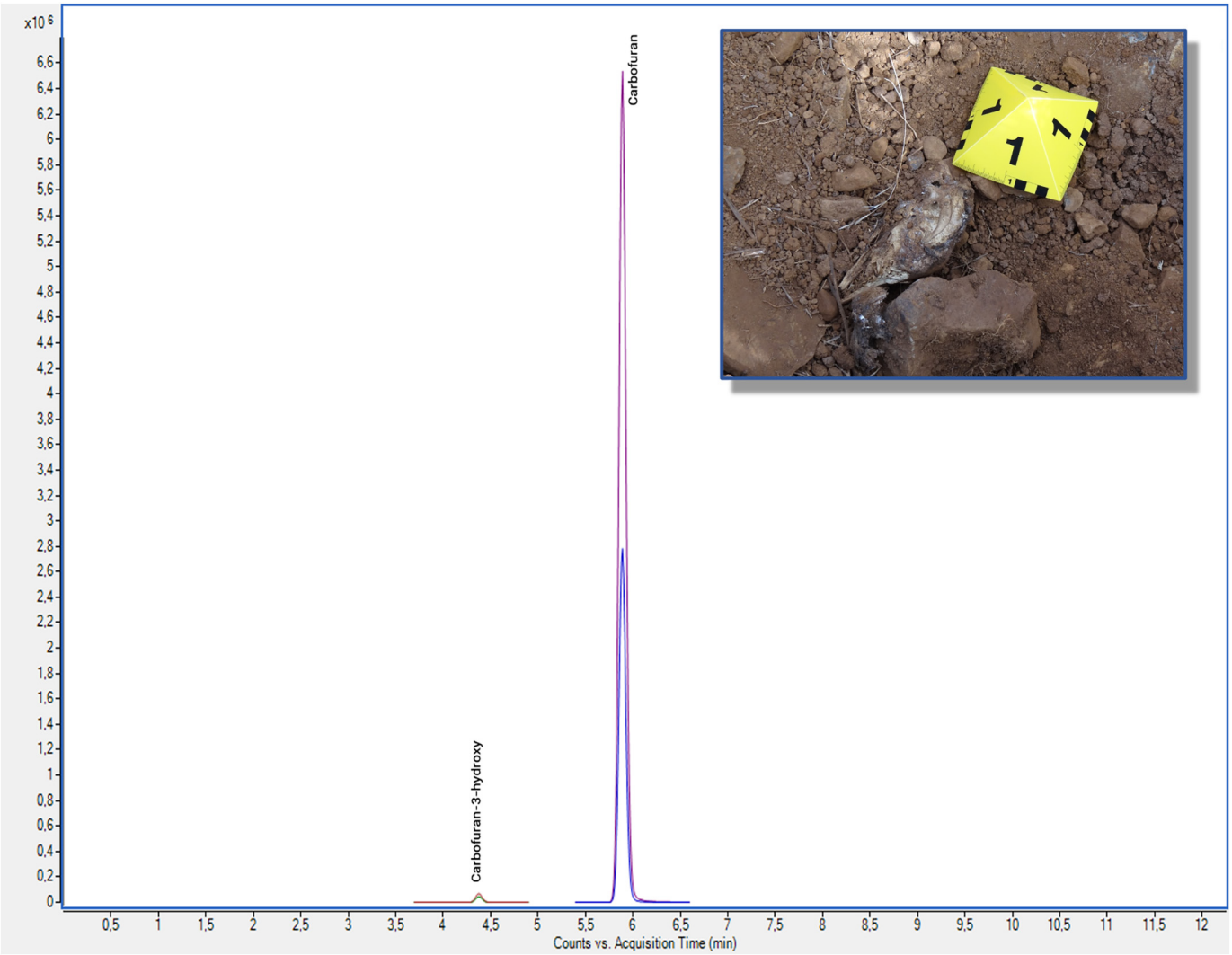


Fig. 5. Chromatogram of the positive identification of carbofuran and 3 hydroxy carbofuran in soil underneath the remains of former dead animals obtained in the context of an environmental forensic investigation.

In Fig. 4 we show the chromatograms corresponding to the analysis of this sample, as an example of the potential of the method we have developed. The residues that have been detected in this sample faithfully reflect the phytosanitary treatment records applied in this farm during the last 10 years. All the residues detected in the sample correspond to pesticides used in the past on the plot. Of the 18 pesticides identified, the highest concentrations (> 100 ng g^{-1}) correspond to pesticides used during the last three seasons, except for cyprodinil (not used on this farm for about 4–5 years) and quinoxyfen, which has been not used for more than 10 years (EC, 2020). Cypermethrin residues correspond to a winter treatment in 2017, since this pesticide has not been applied on the farm since then.

3.4.2. Environmental Forensic Investigation

In this case, we applied the method to two soil samples, collected beneath highly degraded carcass remains and bones of birds of prey that had allegedly died from poisoning in the past. The samples were collected by court order, after a large number of bird and fresh domestic animal carcasses were detected in the area, as well as many dead insects. The aim of the environmental toxicology expert's report was to identify whether the former remains also belonged to animals that may had been poisoned in a previous episode. For this, we analyzed the soil beneath the animal remains in our laboratory. As shown in Fig. 5, the application of the method described here allowed the identification of carbofuran, and 3 hydroxy carbofuran at extremely high concentrations (4198 and 227 ng g^{-1}, respectively). Carbofuran was banned in the EU in 2007, but it has been shown it is still often used for malicious purposes, such as in the preparation of poisoned baits (Ruiz-Suarez et al., 2015). This analysis allowed us to confirm that the alleged poisoner probably acted in the area previously with the same *modus operandi*, since our results on the soil were consistent with the detection of the same compounds in the fresh bird carcasses recently found in the same area.

4. Conclusions

A one-step QuEChERS-based method has been developed and validated for the extraction of 218 pesticides in agricultural soil samples and their analysis by LC-MS/MS and GC–MS/MS. This makes the method a simpler, faster and cheaper process as the need to use more solvents and purification reagents were avoided. A successful linearity, precision, accuracy was obtained for the selected compounds and the LOQ was well below the typically fixed in soil. The method was tested on various farms soil samples and forensic cases and

Table 2
Pesticides and metabolites detected in 18 samples of agricultural soil. Concentrations are expressed in μg kg^{-1}.

Soil sample	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	Frequency
Type of crop/farm	AF [a]	AF [a]	B [b]	B [b]	B [b]	F [c]	F [c]	F [c]	MV [d]	MV [d]	MV [d]	AV [e]	OT [f]	OT [f]	OT [f]	VY [g]	VY [g]	VY [g]	%
4.4′-Dichlorobenzophenone (metabolite of dicofol)			4.93	4.06	2.03	4.86	14.36		94.72	16.29	4.37		4.31		3.80	1.42	0.75	0.68	72.2
4.4′-Dicofol									24.84										5.6
Benalaxyl	1.54															27.05	0.53	0.62	22.2
Boscalid (formely nicobifen)	5.58															536.97	26.68	24.08	22.2
Buprofezin			0.58	0.55	1.20	4.06	0.56		48.54	2.41	3.64								44.4
Chlorpyrifos	4.92															7.75			11.1
Cymoxanil																3.90			5.6
Cypermethrin (sum of four isomers)																108.56			5.6
Cyproconazole (two isomers)															2.94				5.6
Cyprodinil																401.24			5.6
Deltamethrin											902.19								5.6
Endosulfan alfa									19.43	1.49	1.82		51.31		6.74				27.8
Ethion (diethion)																0.57			5.6
Ethoprophos									0.61	0.58									11.1
Fenamiphos				6.15	42.80				2.72		0.58								22.2
Fenamiphos sulfone					0.83						3.81								11.1
Fenamiphos sulfoxide				2.05	6.23				1.96	1.73	4.90								27.8
Fenarimol																8.78			5.6
Fenbutatin oxide			4.79	12.64	8.34	46.69	14.75		385.27	361.86	29.13		9.80		9.36				55.6
Fenpropimorph														6.19					5.6
Hexythiazox									2.95										5.6
Imidacloprid							5.14												5.6
Lufenuron	3.39																		5.6
Mefenoxam (metalaxyl-M)																14.98			5.6
Metalaxyl																12.41			5.6
Methoxyfenozide									1.28										5.6
Metrafenone																488.33	11.26		11.1
Myclobutanil							2.41				2.45								11.1
N·*N*-Dimethyl-N′-p-tolylsulphamide (DMST.metabolite of tolyfluanid)						1.05	2.80												11.1
Oxadixyl															2.09				5.6
Penconazole						0.92	1.64									3.90		0.57	22.2
Permethrin (two isomers)	4.17																		5.6
Procymidone																18.60			5.6
Proquinazid																4.80			5.6
Pyrimethanil																31.43			5.6
Quinoxyfen																390.30	11.35	6.16	16.7
Tetraconazole																9.64			5.6
Triadimefon						1.86	2.57		0.86										16.7
Triadimenol						9.96	35.42		2.68										16.7
Number of residues	5	0	3	5	6	7	9	0	12	6	9	0	3	1	5	18	5	5	

[a] AF: abandoned farmland.
[b] B: banana crop.
[c] F: fruit tree farms.
[d] MV: mixed vegetables farms.
[e] AV: avocado farm;
[f] OT: organic transition farms;
[g] VY: vineyards.

demonstrated to be well suited for monitoring pesticide residues in this matrix.

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142015.

CRediT authorship contribution statement

1. **guarantor of integrity of the entire study:** OPL
2. **study concepts and design:** AAD, OPL
3. **literature research:** AAD, CRB, RDD, MMBS, OPL
4. **laboratory work:** AAD, CRB, RDD, MMBS, OPL
5. **data analysis:** AAD, CRB, OPL
6. **statistical analysis:** AAD, CRB, OPL
7. **manuscript preparation:** AAD, CRB, RDD, MMBS, OPL
8. **manuscript editing:** AAD, CRB, RDD, MMBS, OPL

Declaration of competing interest

The authors declare no conflict of interest. This is an independent research. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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