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Differences in the levels of sulphites and pesticide residues in soils and wines and under organic and conventional production methods

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ABSTRACT

The surface and output of organic agriculture is growing steadily in recent years, being generally seen as a healthier, safer and more sustainable alternative to conventional agriculture. Comparisons between organic and conventional products are nonetheless scarce in the literature, especially in the case of wine. The aim of this study was to compare sulphite content and pesticide residues in both soils and wines under organic and conventional production. Fourteen samples of organic and conventional wines and vineyard soils were collected in pairs for each of the seven wine-producing islands of the Canary Islands. A QuEChERS-based method was employed to detect 218 pesticides and 49 POPs. Sulphites were measured by potentiometric titration with a double electrode. On average, higher levels of sulphites were found in conventional wines. Similarly, conventional wines presented higher numbers and concentrations of pesticide residues both in soils and wines than their organic counterparts. The overall pesticide concentrations in our sample was 4.2 μg/kg. Conventional wines presented a considerably higher average concentration than organic wines (8.2 against 0.25 μg/kg). In turn, concentrations in conventional soils averaged 8.7 against 2.8 μg/kg in organic soils, a 68.19 % lower residue concentration. The analytes most commonly found were PCB 28, p,p′-DDE, tebuconazole and the metabolite 4,4′-dichlorobenzophenone in soils and mefenoxam, tebuconazole, fluopyram and boscalid in wines. No single wine exceeded the 10 % of the MRLs established by the European Union for wine grapes. However, the presence of low levels of pesticides in organic wines should be monitored.

1. Introduction

Vineyards are one of the most pesticide-intensive crops worldwide, concentrating a major share of pesticide use in various European countries (Alonso González et al., 2021). This is due to the susceptibility of the European *Vitis vinifera* grapevine to insects, fungal and viral infections, mainly the grape moth (*Lobesia botrana*), grey mold (*Botrytis cinerea*), downy mildew (*Plasmopara viticola*) and powdery mildew (*Uncinula necator*). The use of pesticides is consequently widespread and high numbers of sprayings are often required to protect the grapevine and successfully achieve quality grapes during harvest. As reported by many authors, pesticide residues are to be found in both organic and conventional wines in different amounts depending on spraying dosage and frequency (Angioni and Dedola, 2013; Santana-Mayor et al., 2020; Schusterova et al., 2021). The latest EU report on pesticide residues in foods clearly reports pesticide residues in grapes: 86 % of the grape samples contained one pesticide, and 68 % contained multiple residues (EFSA et al., 2021). Pesticide residues in wine can also affect its processing and quality parameters (Čuš et al., 2010; Dumitriu et al., 2021a).

Despite this fact, there are no Maximum Residue Limits (MRLs) set for wine at the EU level on the grounds of the rapid dissipation rates of newer pesticides through biotransformation reactions and their biodegradation during winemaking processes, including absorption by lees and pomace, and the use of clarification and filtering products and systems (Angioni and Dedola, 2013; Herrero-Hernández et al., 2013). Only certain countries such as Switzerland and Italy have set MRLs for some pesticides in wine (González-Rodríguez et al., 2009). As a consequence, a 10 % of the MRL established for vinification grapes has been

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commonly agreed upon as a maximum limit for pesticide residue in wines (Pérez-Mayán et al., 2021). The MRLs for grapes typically range between 0.01 mg/kg and 5 mg/kg, although higher limits are allowed for lesser hazardous pesticides. The MRL is not a toxicological limit but instead a combination of agricultural information about efficacy and biodegradation of pesticides with tolerance levels coming from toxicological data sources (Angioni and Dedola, 2013). The combined effect of multiple pesticide residues in human health has not been yet explored in-depth (Rotter et al., 2018).

Beyond wine, soil and groundwater pollution by pesticides also represents a growing concern (Schreck et al., 2008), most importantly because vineyards are highly susceptible to soil degradation and erosion (Komárek et al., 2010; Pose-Juan et al., 2015). Pesticides come from different chemical classes and undergo manifold processes of transport, degradation and absorption, interacting with soil microorganisms and altering enzymatic activity (Muñoz-Leoz et al., 2013), causing diffuse pollution to the environment (Stolte et al., 2015). The notion of "soil memory" emphasizes the need for long-term strategies to remediate degraded soils and their environmental consequences (Farlin et al., 2013). It also has methodological consequences because long-term pesticide contamination of soils may affect current crops, including those with an organic certification (Geissen et al., 2021). Understanding previous soil uses becomes a prerequisite for successfully understanding soil composition today (Alengebawy et al., 2021). Furthermore, comparing soil and wine pesticide residues allows for a better understanding of controversial issues in organic agriculture such as fraud or cross-contamination (Provost and Pedneault, 2016). Differing results in soils and wines may be suggestive of cross-contamination or indicate long-term soil pollution in organic plots.

From the consumer side, recent European Union surveys show that pesticide residues rank among the highest food safety concerns (EFSA, 2019), while sulphites are a significant concern among wine drinkers (Amato et al., 2017). Organic food is generally perceived as safer, healthier and better for the environment, with greater nutritional value and fewer toxic substances (Hemmerling et al., 2015). More sustainable productive alternatives are growing market share and institutional support in the EU. Organic wine is the most widespread and well-known. It forbids the use of synthetic pesticides, replacing them with some inorganic compounds (copper or sulphur) and active substances such as spinosad, deltamethrin or lambda-cyhalothrin (European Commission, 2012). Organic regulations also limit the use of oenological additives (Alonso González and Parga-Dans, 2018).

The surface and share of organic viticulture has steadily grown in recent years, Spain boasting the largest organic vineyard area globally with 121,279 ha and a 12.73 % of vineyards in organic (MAGRAMA, 2020). In comparison, only 404 ha or 5.1 % of the Canary vineyards are certified organic, with 27 organic cellars registered. Moreover, the islands have witnessed an stagnation in the conversion to organic viticulture since the 2010 s, and the archipelago remains the most pesticide-intensive region in Spain in terms of kilograms of active substances applied per hectare (Alonso González et al., 2021). For example, against 5.2 and 5.4 kg/ha in peninsular Spain, the Canaries used 69.9 and 69.1 kg/ha respectively in 2012 and 2016 (MAPAMA, 2018), although recent analyses suggest that these figures may be even higher (Alonso González et al., 2021). The consequences for human health are potentially harmful, as shown by studies detecting an average of six different non-persistent pesticide residues in more than 99 % of a sample of non-exposed adults in the larger island of Tenerife (Zumbado et al., 2005).

Therefore, reliable residue data analysis can be of great value in this region, indicating possible pesticide risk exposure on human health. To date, studies comparing organic and conventional foods in the archipelago have only focused on dairy products and eggs (Luzardo et al., 2012, 2013). Comparative analyses focusing on soil have not yet been implemented in the islands, mainly because there are no requirements for pesticide monitoring in the EU, contrary to water or food monitoring. The volcanic character of the Canary Island can make results generalized to other volcanic regions worldwide. The aim of this study was to analyze 218 pesticides and 49 persistent organic pollutants (POPs) found in the soils of vineyards and wines of organic and conventionally produced wines for the first time, as well as total sulphite levels, from each of the seven wine-producing islands of the Canary archipelago. In order to understand the soil history of the vineyards, the study analyzed current fungicides and insecticides, residues, but also the presence of older organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). In doing so, it increases the knowledge about conventional and organic wines in the Canary Islands and beyond.

2. Materials and methods

2.1. Sample collection

A total of 14 wines, two per wine-producing island were chosen during the vintage 2019–2020. Detailed information about each wine is provided in Table 1. Wine names were coded according to the island of origin and production method. Their original names and geolocation remains hidden for privacy purposes. The sampling strategy consisted of choosing pairs of organic and conventional wines produced from vineyards as close as possible to each other, producing the same wine grape variety, mostly in a radius of a few km, to minimise differences in environmental, soil and climate characteristics. Different winemaking methods were also taken into account and a total of six red and eight white wines were selected. The sampling also prioritised pairs of wines with similar profiles in terms of alcohol volume, residual sugar, harvest year, grape variety and ageing techniques and materials employed (mostly stainless steel tanks). Most wines were dry, except the conventional sample from El Hierro, a sweet wine analysed owing to the lack of alternative wine samples in the area. All wines came from protected designations of origin except the organic wine samples from Tenerife and Fuerteventura. All samples were collected personally in the cellars, from commercially available bottles rather than wines stored in cellars until commercialisation. All organic wines were certified by the Canary Institute of Agrofood Quality (ICCA) under the EU organic agriculture scheme. The organic samples from Tenerife and La Gomera were in their second year of the compulsory transition period to organic agriculture when samples were collected. All samples were transferred to plastic containers after the original bottles were opened, and stored at 4–5ºC until analysis.

2.2. Pesticide and POP residues analyses

2.2.1. Reagents and chemicals

Analytical-grade acetonitrile (ACN), acetone (Ac), and formic acid (FA, HCOOH) were purchased from Honeywell (Morristown, NJ, USA). Salts for extraction based on the AOAC QuEChERS method (Lehotay, 2007) were purchased in commercial premixes from Agilent Technologies (6 g $MgSO_4$ and 1.5 g CH_3COONa) (Palo Alto, CA, USA).

Certified standards stock mix solutions of pesticides included in the multi-annual plan of the EU and selected POPs were purchased from CPA Chem (Stara Zagora, Bulgaria) in 10 mixes of compatible pesticides at 10 μg/mL in acetonitrile (ACN) and in 5 mixes for POPs, each of them at 100 μg/mL: one for the OCPs (in acetone), one for the PAHs (in dichloromethane), one for the PBDEs (in iso-octane) and two for PCBs (in iso-octane). Additionally, individual certified standards of a selection of pesticides (purity 95.19–99.9 %) were acquired from Dr. Ehrenstorfer (Augsburg, Germany) and Sigma-Aldrich (Augsburg, Germany). Isotopically labelled compounds (Atrazine-d5, Carbendazim-d3, Chlorpyrifos-d10, Cyromazine-d4, Diazinon-d10, Linuron-d3, Pirimicarb-d6) and PCB 200 used as procedural internal standards (P-IS) were obtained from Dr. Ehrenstorfer and Sigma-Aldrich, (99.3–99.9 % purity). Individual stock standard solutions at 1000 μg/mL were prepared for P-IS

Table 1
Sample description including codification, island, type of wine, production method, harvest, grape variety, location, and geological substrate.

Sample	Island	Type	Production	Harvest	Variety	Site
TF1	Tenerife	Red	Organic	2019	Listán Negro	La Perdoma
TF2	Tenerife	Red	Conventional	2019	Listán Negro	La Perdoma
LP1	La Palma	White	Organic	2019	Albillo Criollo	Puntagorda
LP2	La Palma	White	Conventional	2019	Albillo Criollo, Listán Blanco	Tijarafe
GC1	Gran Canaria	Red	Organic	2019	Listán Negro, Castellana	Vega de Gáldar
GC2	Gran Canaria	Red	Conventional	2019	Listán Negro	Vega de Gáldar
LG1	La Gomera	White	Organic	2019	Forastera Gomera	Igualero
LG2	La Gomera	White	Conventional	2019	Forastera Gomera	El Cercado
FT1	Fuerteventura	White	Organic	2019	Marmajuelo, Malvasía	Casillas de Morales
FT2	Fuerteventura	White	Conventional	2019	Malvasía	Lajares
EH1	El Hierro	White	Organic	2019	Verijadiego, Pedro Ximenez, Listán Blanco	Frontera
EH2	El Hierro	White	Conventional	2019	Verijadiego	Frontera
LZ1	Lanzarote	Red	Organic	2019	Listán Negro, Syrah	La Geria
LZ2	Lanzarote	Red	Conventional	2019	Listán Negro, Syrah, Tintilla, Merlot	La Geria

and additional pesticides in ACN. From them, mixed stock and working solutions were prepared at 10 and 1 μg/mL for those pesticides and P-IS, respectively. A working solution containing all the pesticides at a final concentration of 0.833 μg/mL was prepared by mixing the ten parts of the European Commission commercial mix and an additional in-house solution containing the rest of the pesticides (10 μg/mL/each). For the POPs, an intermediate solution containing all the analytes at a final concentration of 20 μg/mL/each was prepared by mixing the five parts of the commercial mix, from which a working mix solution was prepared at 1 μg/mL in Ac.

2.2.2. Sample preparation

2.2.2.1. Soil samples. Soil sample analysis was performed with a previously validated method for the extraction of 218 pesticides and 49 POPs in agricultural soils based on the well-known QuEChERS procedure (Acosta-Dacal et al., 2021a, 2021b; Lehotay, 2007). Briefly, 10 g of soil were mixed with 10 mL of ACN-2.5 % FA in a 50 mL centrifuge tube and shaken vigorously for 1 min. Next, 6 g of $MgSO_4$ and 1.5 g of CH_3COONa were added, shaken vigorously for another min and then sonicated for 15 min in an ultrasonic bath (VWR, Radnor, Pennsylvania, United States). After that, samples were placed in a rotatory shaker (Ovan, Barcelona, Spain) for 25 min. Next, they were centrifuged for 10 min at 4200 rpm (3175.16xg) in a 5804 R 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 either directly analyzed in GC-MS/MS or diluted with ultrapure water (1:1, v/v) and analyzed in LC-MS/MS.

Quality Control samples (QCs) were spiked with the required volume to achieve a concentration of 20 ng/mL of the standard mix solutions and were left to stand for 1 h prior to extraction. In the same step, all samples, QCs and blanks were added 50 μl of P-IS mix solution.

2.2.2.2. Wine samples. A method also based on the QuEChERS technique was used to extract the wine samples. Into a 15 mL centrifuge tube 1 mL of wine was extracted with 2 mL of ACN-1 % FA, shaken vigorously for 1 min and then sonicated for 20 min in an ultrasonic bath. Next, 6 g of $MgSO_4$ and 1.5 g of CH_3COONa were added and shaken vigorously for another min. After that, they were centrifuged for 10 min at 4200 rpm (3175.16xg). Finally, an aliquot of supernatant extract was filtered through 0.20 μm and was either directly analyzed by GC-MS/MS or LC-MS/MS.

2.2.3. Instrumental analyses

The analyses of the pesticides and POPs in soil and wine samples was performed by gas and liquid chromatography coupled with triple quadrupole mass spectrometry (GC-MS/MS and LC-MS/MS). The retention times, precursor, fragment ions, and collision energies for each compound and equipment have been previously published and are given as Supplementary material in Table S1 (Acosta-Dacal et al., 2021a).

The GC-MS/MS analysis was performed with a GC System 7890B equipped with a 7693 Autosampler and Triple Quad 7010 mass spectrometer (Agilent Technologies, Palo Alto, USA). The chromatographic separations were performed using 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) to use of the back-flushing technique. Helium (99.999 % purity, Linde, Dublin, Ireland) 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 temperatures of the GC oven were programmed as follows: a) initial temperature: 80 °C for 1.8 min; b) ramp 1: 40 °C/min to 170 °C; c) ramp 2: 10 °C/min to 310 °C; d) hold time: 3 min. Post- run backflush was set at − 5.8 mL/min and 315 °C for 5 min. Total run time was 20.75 min. MS/MS analyses were performed using electron impact (EI) ionization source in multiple reaction monitoring (MRM) mode, using 24-time segments. 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. The transfer line and injector temperature were 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.

The LC-MSMS analysis was conducted using a 1290 Infinity II LC System coupled to a Triple Quad 6460 mass spectrometer (Agilent Technologies, Palo Alto, CA, USA). 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 was used for the chromatographic separation. The mobile phases were 2 mM ammonium acetate 0.1 % FA in ultrapure water (A) and 2 mM 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 - 10–14 min; 5 % B - 14.01 min. The flow rate was set at 0.4 mL min − 1, the volume injected was 5 μl and the total run time was 18 min. 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 6.0 (99.9999 % purity, Linde, Dublin, Ireland) was used as collision gas. The sheath gas was set at 12 L min − 1 at 330 °C. 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. Data analysis for both GC-MS/MS and LC-MS/MS was performed using Agilent software MassHunter Quantitative

Analysis (for QQQ) vB.07.01 and MassHunter Qualitative Analysis vB.07.00.

2.3. Determination of sulphite concentration

Total sulphite determination was carried out following the Ripper method. This working procedure involves the titration of sulfur dioxide in wines with iodine (Araújo et al., 1998). The method is based on a redox reaction of Sulphur dioxide and iodine that results in the reduction of iodine and the formation of sulphate anion, followed by a blue coloration of the mixture. A double platinum electrode Crisson SO_2 Matic 23 was employed.

2.4. Statistical analysis

The significance of organic vs conventional production systems was assessed by comparing combined data for each practice and by analysing data from each particular island in pairs. Statistical analysis was performed using Microsoft Excel software (Microsoft Corp., Redmond, WA, USA). Pair comparison was completed employing student's t-test at the level of significance $p \leq 0.05$.

3. Results and discussion

Seven pairs of conventional and organic wines totalling 14 samples from each wine-producing island of the Canary archipelago were analyzed for sulphite concentration and pesticide residues in soil and wine. Based on our results, we discuss potential determinants for differences between both productive types and assess their impact in soils and wines, comparing residue levels with current MRLs in the European Union to examine their safety.

3.1. Sulphites

Sulphite addition is a commonplace oenological practice throughout the world, well-known by consumers thanks to the legal requirement to label it (Alonso González and Parga-Dans, 2018). Sulphating compounds are used against oxidation and bacterial proliferation that could lead to wine spoilage, thanks to their affordability and ease of application. Sulphites can appear in free and bound states in wine, forming hydroxysulphonate complexes with carbonyl groups (Čepo et al., 2018). Free sulphites are of oenological interest as they reflect their anti-oxidant potential. However, total sulphites are of toxicological interest because these will be present in the final product and reach consumers. Sulphites are potentially damaging for human health (Garcia-Fuentes et al., 2015). They can inhibit growth of beneficial bacteria in the gut and cause irritation and reactions to asthmatic and allergic people (Irwin et al., 2017). Consequently, alternatives for the use of sulphites in winemaking are on the rise in the market, as well as consumer awareness on the subject (Alonso González and Parga-Dans, 2020).

In the EU, the maximum sulphite levels for organic wine are 50 mg per liter lower than those allowed for conventional dry wines (residual sugar level below 2 mg/L) and 30 mg lower per liter for sweet wines. This means that for organic dry red wine a sulphite content of up to 100 mg/L is allowed, while organic dry white and rosé wines could have up to 150 mg/L of sulphites added. These levels are still relatively high and other certifications such as the biodynamic label "Demeter" are more restrictive in this regard. It is not therefore surprising that sulphite levels do not vary much between organic and conventional wines as reported in the literature (Čepo et al., 2018; Cravero, 2019). Our results show that all samples were within permissible levels (see Table 2). The highest total sulphite concentration was found in a conventional white wine from Fuerteventura (122.3 mg/L). Conventional wines presented slightly higher total sulphite levels than their organic counterparts (55.6 vs 76.5 mg/L). In line with the previous literature on the topic, red wines presented rather lower sulphite concentration than whites (36 vs 88.6 mg/L). In light of these results, sulphites should not be considered a key differential marker between organic and conventional wines.

Table 2
Mean total sulphite concentrations in white and red organic and conventional wines.

Type	Sample	Concentration & Standard Deviation (mg/l)
Organic	Average	55.6 ± 37
	TF1 (Red)	8 ± 1.7
	LP1 (White)	105. 7 ± 1.3
	GC1 (Red)	28. 7 ± 0.6
	LG1 (White)	72.00
	FT1 (White)	18.7 ± 2. 9
	EH1 (White)	86.3 ± 3.8
	LZ1 (Red)	70 ± 4.4
Conventional	Average	76.5 ± 42
	TF2 (Red)	13.3 ± 1.5
	LP2 (White)	99.3 ± 2.3
	GC2 (Red)	32.7 ± 0.6
	LG2 (White)	83.3 ± 2.3
	FT2 (White)	122 ± 1.3
	EH2 (White)	121 ± 1
	LZ2 (Red)	63.7 ± 2.1
Red Wines	Average	36.1 ± 26
White Wines	Average	88.6 ± 33

Not detected (ND) and average concentrations (mean ± SD) of pesticide residues in wine samples expressed in μg/kg (n = 14).

3.2. Pesticide residues in wine

Our analysis revealed the presence of 25 different pesticides in wines (see Table 3). Pesticide residues and their abundance are intrinsically related with the climatic conditions for wine production (Esteve-Turrillas et al., 2016). Earlier studies tended to report lower pesticide levels because the number of substances analyzed was significantly lower, as in the study conducted by Guidotti et al. (1998) reporting that 43 % of wines were clean.

In our case, only 21.4 % of wines were free of pesticides, while 35.7 % presented six or more residues. This is in line with a recent analysis of

Table 3
Not detected (ND) and average concentrations (mean ± SD) of pesticide residues in wine samples expressed in μg/kg (n = 14).

Pesticide	Organic	Conventional	Total
Average	0.25	8.20	4.22
Acetamiprid	ND	0.65 ± 1.1	0.32 ± 0.8
Azoxystrobin	0.04 ± 0.1	3.2 ± 8.5	1.6 ± 6
Boscalid	ND	26.7 ± 54	13.3 ± 39
Chlorantraniliprole	ND	0.06 ± 0.16	0.03 ± 0.11
Dimethoate	ND	0.12 ± 0.32	0.06 ± 0.2
Dimethomorph	ND	0.16 ± 0.21	0.08 ± 0.2
Fluopyiram	0.70 ± 1.9	15.3 ± 27	8 ± 20
Iprovalicarb	ND	3 ± 5.5	1.5 ± 4
Kresoxim-methyl	ND	1.8 ± 4.1	0.88 ± 3
Mandipropamid	ND	0.06 ± 0.2	0.03 ± 0.1
Mefenoxam (metalaxyl-M)	0.14 ± 0.3	9.5 ± 18	4.82 ± 13
Metalaxyl	ND	11.4 ± 25	5.71 ± 18
Methiocarb	0.84 ± 2.2	ND	0.42 ± 1.6
Methiocarb-sulfoxide	4 ± 11	ND	2 ± 7. 6
Metrafenone	ND	1.2 ± 3	0.59 ± 2.2
Myclobutanil	ND	2.4 ± 5	1.2 ± 3.7
Penconazole	ND	0.09 ± 0.2	0.04 ± 0.2
Phthalimide (Folpet deg)	ND	44.2 ± 100	22 ± 72
Pyrimethanil	0.52 ± 1.4	0.87 ± 1.6	0.7 ± 1.4
Tebuconazole	0.21 ± 0.42	21.9 ± 26	11 ± 21
Tetraconazole	ND	0.47 ± 1.2	0.2 ± 0.9
Triadimenol	ND	8.5 ± 17	4.2 ± 12
Trifloxystrobin	ND	0.05 ± 0.1	0.03 ± 0.10
Fenhexamid	ND	61 ± 155	30 ± 110
Thiophanate-methyl	ND	0.60 ± 1.6	0.30 ± 1.1

conventional red wines including the Canary Islands, where 52 % of the samples presented six or more residues and an overall higher number and variety of pesticides than wines from peninsular Spain (Santana-Mayor et al., 2020). Our results confirm this extent, as wines from both northern (Pérez-Mayán et al., 2021; Pérez-Ortega et al., 2012; Rodríguez-Cabo et al., 2016) and southern Spain (Romero-González et al., 2011) present overall lower detection levels.

Among organic wines, nine residues of seven different pesticides were detected in four samples, while three samples were residue-free. Two samples presented three pesticides, one sample two, and another sample one residue only. Tebuconazole was the only pesticide present in two samples. The other pesticides detected were azoxystrobin, fluopyram, mefenoxam (metalaxyl-M), methiocarb (and its main metabolite methiocarb-sulfoxide) and pyrimethanil, all at low concentrations. In turn, all conventional wines presented residues totalling 49 residues detected of 25 different pesticides. As seen in Fig. 1, the highest number of residues were found in sample LZ2 (11), while two other samples presented ten different residues (EH2 and TF2). Overall, red wines presented more pesticides than whites per sample (5 vs 3.37), but lower average concentrations (1.96 per 7.25 μg/kg). The higher number of pesticides in reds has been repeatedly seen in the literature, most likely because skins are removed from white wines prior to fermentation and therefore transfer less residues from grape to wine than reds (Dumitriu et al., 2021b). However, a lower average concentration for reds is not common in the literature.

The most common residues found in conventional wines were mefenoxam (metalaxyl-M) and tebuconazole (5 samples), fluopyram and boscalid (4). These are fungicides and insecticides commonly used against grey mold (botrytis) and powdery mildew (tebuconazol and fluopyram), and downy mildew (mefenoxam and boscalid). The average concentration of mefenoxam was 9.5 μg/kg, for tebuconazole 21.9 μg/kg, while for fluopyram and boscalid it was 15 μg/kg and 26.7 μg/kg respectively. Organic wines were free from boscalid and contained low concentrations of tebuconazole (0.21 μg/kg), fluopyram (0.70 μg/kg) and metalaxyl (0.14 μg/kg). The overall pesticide concentrations in our sample was 4.2 μg/kg. Conventional wines presented a considerably higher average concentration than organic wines (8.2 against 0.25 μg/kg). Pesticide concentrations over 100 μg/kg detected in individual samples occurred in conventional wines only, namely 146.34 μg/kg for boscalid (FT2), 268.8 μg/kg for phtalimide (GC2) and 411.6 μg/kg for fenhexamid (TF2). A 21.42 % of the samples contained residues higher than 100 μg/kg, much higher than the 8.4 % found by Esteve-Turrillas et. al (2016) in their study of international wines or the 7.5 % detected by Čuš et al. (2022) in Slovenian wines.

In line with the literature, boscalid is frequently found in the highest proportions, but other common pesticides reported such as fenhexamid, dimethomorph or pyrimethanil do not rank among the top pesticide residues in our study (Esteve-Turrillas et al., 2016). In the study on

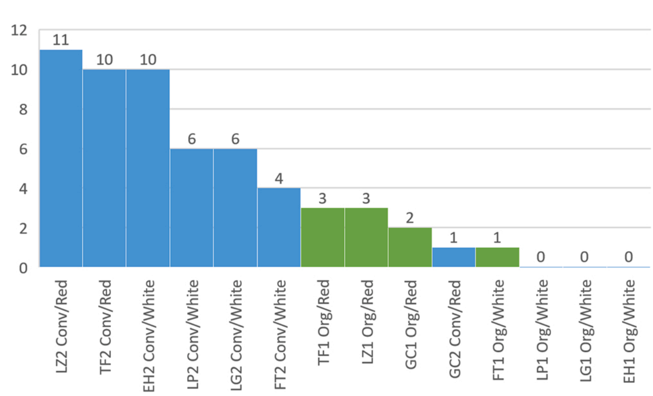

Fig. 1. Number of different pesticides detected in conventional (blue) and organic (green) wines per sample.

wines under Integrated Pest Management strategies by Angioni and Dedola (Angioni and Dedola, 2013), the pesticides with higher levels reported were of metalaxyl (54.5 % of the sample), which is in line with our study. In the Canary Islands, an analysis of 11 pesticides among homemade wines found procymidone to be the commonest residue (Ravelo-Pérez et al., 2008). More recently, Santana-Mayor (2020) found tebuconazole, boscalid, carbendazim, metalaxyl, iprodione, dimethomorph, thiophanate-methyl and pyrimethanil to be the most abundant pesticides in Canary red wines, which is in agreement with our results.

The mean concentrations of pesticide residues are presented in Table 3. As can be observed, both the total number and the average levels of pesticides were considerably lower in organic wines than in their conventional counterparts. This is in agreement with the previous literature. For instance, Vitali Čepo et al. (2018) found rather lower concentrations and average lower number of pesticides per sample in organic than conventional Croatian wines. Nonetheless, in our study, all wines can be considered as safe and no exceedance of the maximum residue limits was found in any tested sample. As previously mentioned, there are no regulated MRLs for wine (European Parliament, 2005). We checked all residues against the 10 % of MRLs established for wine grapes, in line with previous works (Pérez-Mayán et al., 2021). This limit has been calculated taking into consideration the processing factor, that is, the ratio of losses in the concentration of a chemical from raw material (grape) to wine. This includes the pesticide loses in the cake and lees, as well as in the processing including clarification and filtration (Corrias et al., 2021). Despite wines are below MRLs and are safe for human consumption, the presence of unauthorised pesticides or their metabolites in organic wines is a matter of concern. In our samples, a 42.8 % of organic wines contained pesticide residues, while previous studies detected proportions of up to 15 % and 20 % (Čepo et al., 2018; Cravero, 2019; Schusterova et al., 2021) or no pesticides at all (Dutra et al., 2018). As reported by other authors, the presence of pesticides in organic foodstuffs can derive both from cross-contamination because the location nearby conventional farms or from environmental context including ground water, soil or rain (Gómez-Ramos et al., 2020).

3.3. Pesticide residues in soil

As mentioned earlier, there are no requirements for monitoring pesticide residues in soil at the EU level. However, recurrent pesticide applications lead to long-term environmental and underground water pollution, as it has been estimated that only 0.1 % of their compounds reaches the crops thus entering the environment (Pimentel and Burgess, 2014). Many complex factors explain the half-life of pesticides in the environment and the processes of mobility, degradation and adsorption, including their chemical properties, frequency and concentrations applied, soil and climatic context (Pose-Juan et al., 2015). Our analysis detected 63 different quantifiable residues occurring 189 times in 14 samples of vineyard soils, with an overall average of 5.8 μg/kg (see Table 4). No samples were free of residues and 57.14 % of them contained 10 or more residues. The most frequent residues overall were PCB28 (present in 10 samples), folpet (10), the DDT metabolite dichlorodiphenyldichloroethylene p,p′ DDE (10), tebuconazole (8), another DDT metabolite, 4,4′-Dichlorobenzophenone (8), metalaxyl (7) and triadimenol (7). One sample contained 35 different residues (TF2).

As seen in Fig. 2, the island where a highest number of pesticides were detected was Tenerife (61), followed by Gran Canaria (34). These are the larger and more intensively exploited islands in the archipelago, which explains a greater bioaccumulation of residues compared to other minor islands. Therefore, pesticide residues reveal the memory of agricultural soils. This is clearly revealed by the presence of residues of Polychlorinated Biphenyls (PCBs) and Organochlorine Pesticides (OCPs). PCBs were banned in the US in the 1979 and in 1987 in the EU but their presence is still clear in our analysis. In turn there are OCP residues from DDT metabolites (banned in 1983 in the EU), lindane (banned in 2008 in the EU) and dieldrin (banned in 1994 in Spain). In

Table 4
Not detected (ND) and average concentrations (mean ± SD) of pesticide residues in soil samples expressed in μg/kg (n = 14).

Pesticide / Contaminant	Organic	Conventional	Total
Average	2.78	8.7	5.76
4,4′-Dichlorobenzophenone	2 ± 3	2 ± 2.8	2 ± 2.8
4,4′-Dicofol	0.53 ± 1	1.3 ± 3.3	0. 9 ± 2.5
Azoxystrobin	ND	0.03 ± 0.07	0.01 ± 0.05
Benalaxyl	0.06 ± 0.2	6.9 ± 14.2	3.5 ± 10.3
Boscalid	10 ± 28	132 ± 307	71.3 ± 219
Buprofezin	0.05 ± 0.1	ND	0.02 ± 0.2
Chlorantraniliprole	0.20 ± 0.5	ND	0.10 ± 0.4
Chlorfenapyr	0.49 ± 1.3	0.3 ± 0.7	0.38 ± 1
Chlorpyrifos	ND	0.7 ± 1.4	0.36 ± 1
Cymoxanil	ND	2.3 ± 5.6	1.2 ± 4
Cypermethrin	ND	1.8 ± 4.7	0.89 ± 3.3
Cyproconazole	ND	1.4 ± 3.7	0.70 ± 2.6
Cyprodinil	0.15 ± 0.4	0.06 ± 0.2	0.11 ± 0.3
Diazinon	0.17 ± 0.4	ND	0.08 ± 0.3
Dimethomorph	0.14 ± 0.4	0.08 ± 0.2	0.11 ± 0.3
Endosulfan alfa	0.07 ± 0.2	ND	0.04 ± 0.1
Fenamiphos sulfoxide	0.03 ± 0.1	ND	0.02 ± 0.06
Fenarimol	0.38 ± 0.6	2 ± 2.3	1.2 ± 1.8
Fenbutatin oxide	2.7 ± 6.2	1.3 ± 2.2	2 ± 4.5
Fipronil sulfide	0.38 ± 1	ND	0.19 ± 0.7
Fluopyram	0.02 ± 0.05	12.2 ± 22.5	6.1 ± 16
Imidacloprid	0.1 ± 0.3	1.8 ± 3.4	0.94 ± 2.5
Indoxacarb	0.24 ± 0.6	ND	0.12 ± 0.4
Iprodione	ND	2.2 ± 5.8	1.1 ± 4.1
Iprovalicarb	ND	4.2 ± 9.3	2.1 ± 6.6
Lufenuron	0.26 ± 0.7	0.19 ± 0.5	0.23 ± 0.6
Mefenoxam (metalaxyl-M)	0.05 ± 0.1	9.4 ± 19.8	4.7 ± 14
Metalaxyl	0.15 ± 0.3	18.9 ± 42.2	9.5 ± 30.3
Methiocarb sulfoxide	0.02 ± 0.05	ND	0.01 ± 0.04
Metrafenone	0.83 ± 2.2	21 ± 53.9	10.8 ± 38
Mevinphos (phosdrin)	ND	0.03 ± 0.08	0.01 ± 0.05
Myclobutanil	ND	20 ± 49.3	10 ± 35
Oxadixyl	ND	0.13 ± 0.4	0.07 ± 0.2
Oxyfluorfen	ND	21.8 ± 49.9	10.9 ± 35.7
Penconazole	0.07 ± 0.2	15.2 ± 28.3	7.6 ± 21
Phthalimide (Folpet deg)	3.6 ± 3.4	2.7 ± 3.5	3.1 ± 3.3
Procymidone	1.9 ± 4.7	1.5 ± 3.4	1.7 ± 4
Propoxur	0.03 ± 0.04	0.09 ± 0.2	0.06 ± 0.1
Pyraclostrobin	0.17 ± 0.3	0.04 ± 0.1	0.11 ± 0.2
Pyridaben	ND	0.02 ± 0.05	0.01 ± 0.04
Pyrimethanil	0.28 ± 0.3	0.26 ± 0.7	0.27 ± 0.7
Pyriproxifen	ND	0.65 ± 1.7	0.32 ± 1.2
Quinoxyfen	0.06 ± 0.2	0.06 ± 0.16	0.06 ± 0.2
Spirotetramat-enol	0.08 ± 0.1	ND	0.04 ± 0.1
Tebuconazole	0.26 ± 0.6	87.1 ± 139	43.7 ± 105
Tetraconazole	0.65 ± 1.4	2.8 ± 4.7	1.7 ± 3.5
Tetradifon	ND	0.39 ± 1	0.19 ± 0.7
Triadimefon	ND	0.70 ± 1.3	0.35 ± 0.9
Triadimenol	0.21 ± 0.4	111 ± 215	55.7 ± 157
Trifloxystrobin	ND	0.16 ± 0.3	0.08 ± 0.2
Dichlorodiphenyldichloroethane (p,p′ DDD)	30.3 ± 66	13.6 ± 35	22 ± 51
Hexachlorocyclohexane (gamma, lindane)	0.86 ± 2.3	ND	0.43 ± 1.6
Dichlorodiphenyldichloroethylene (p,p′ DDE)	93.6 ± 159	37.3 ± 91	65 ± 128
Dieldrin	2.4 ± 6.4	ND	1.2 ± 4.5
Anthracene	0.61 ± 1.6	ND	0.3 ± 1.1
Phenanthrene	1.2 ± 2.8	0.6 ± 1	0.9 ± 2
Fluoranthene	2.4 ± 6.5	0.4 ± 0.9	1.4 ± 4.5
Pyrene	2.5 ± 6.5	0.6 ± 1	1.5 ± 4.6
Benzo[*a*]anthracene	2.3 ± 6.2	0.7 ± 1.9	1.5 ± 4.4
Chrysene	2.6 ± 6.8	0.7 ± 1.9	1.7 ± 4.9
Benzo[*b*]fluoranthene	6.5 ± 15	1.5 ± 3.6	4 ± 11
PCB 28	0.09 ± 0.10	0.07 ± 0.1	0.08 ± 0.1

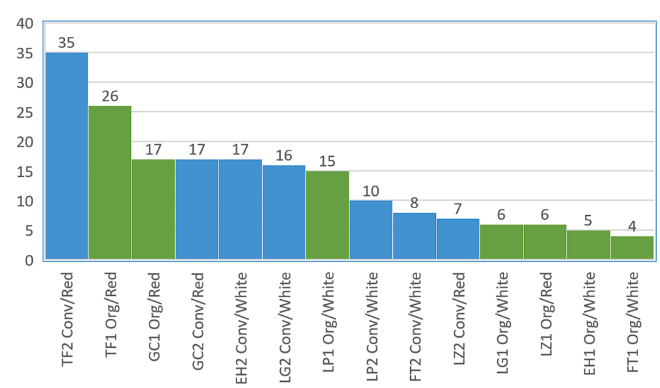

Fig. 2. Number of different pesticides detected in conventional (blue) and organic (green) soils per sample.

the Canary Islands, OCPs were extensively used in banana and tomato crops whose pollution remains until our days. Moreover, OCPs present in the soil have been shown to enter the food chain appearing in other products such as cheese (Almeida-González et al., 2012), and ultimately in human serum (Boada et al., 2012).

Another set of residues present in our sample are polycyclic aromatic hydrocarbons (PAHs). Those compounds mostly derive from combustion processes and are not directly related to pesticide application. PAH levels in crops and foodstuffs have been correlated with the concentration of their particles in the air of a region reaching the soil via precipitation and direct exposure (Roszko et al., 2020). The most frequent PAH detected was phenanthrene, but others such as pyrene or chrysene appear in various samples at low levels. The sample with the highest PAH occurrence and concentration by far was GC1, which can be explained by the presence of a nearby highway.

Differences between organic and conventional management were again patent. In conventional soils, 109 residues of 50 different substances were detected compared with 78 residues of 45 substances in organic soils. Concentrations in conventional soils averaged 8.7 against 2.8 μg/kg in organic soils, a 68.19 % lower residue concentration that is in line with the few available international studies on the topic (Geissen et al., 2021). Five conventional samples presented more than 10 different residues against three organic samples. The prevailing residues in conventional samples were, in descending order, tebuconazole (6), phtalimide, folpet degradation product (5), metalaxyl (5), triadimenol (5) and p,p′ DDE (5). Interestingly, only one contemporary pesticide residue was found in higher levels, namely phthalimide (Folpet), while most residues detected were PCB28 (6) and DDT metabolites including p,p′ DDE (5) and p,p′ DDD (4). Concentrations exceeding 100 μg/kg were detected in 13 occasions, with the highest concentration found in FT2 (823.7 μg/kg for boscalid). Similar levels of these contaminants have been found in a recent study comparing organic and conventional vegetable farms in the Canary Islands (Acosta-Dacal et al., 2021a). These results show that soil restoration is a long-term process that can affect organic producers and the quality of their products, also becoming a source of cross-contamination (Khalid et al., 2020). Another conclusion in line with the literature is that levels of pesticides in soil are much higher than in wine (Corrias et al., 2021; Dumitriu et al., 2021a). Various production processes, from harvesting and transportation into the winery and the winemaking process itself lead to the degradation of pesticides and their biotransformation, influenced by environmental conditions such as sunlight, temperature or humidity. In the cellar, winemaking processes degrade or remove pesticides, mainly fermentation and clarification with various forms of clays.

4. Conclusion

There is a scarce but growing body of literature comparing organic and conventional wines, and in particular levels of pesticide residues and sulphites. Pesticide residues are of increasing concern for consumers and their regulation has international implications for producers and government agencies alike. The data presented here advance knowledge on potential environmental and human risks and offers useful practical advice for the reduction of residues and increased food safety. This study confirms the general trend showing lower numbers and concentrations of pesticide and contaminant residues in organic wines against their conventional counterparts. However, it also reveals the presence of unauthorised residues in some organic wines at low concentrations, probably as a result of cross-contamination or drift processes. This should be an issue to be closely monitored by regulating bodies of organic agriculture to better meet consumer expectations of pesticide free wines. Another remarkable conclusion is that wines from the Canary Islands contain higher numbers and concentrations of pesticides than their counterparts in Spain's mainland and international wines overall. Therefore, strategies to reduce the frequency and occurrence of most pesticides in the vineyards should be implemented, especially in periods closer to harvest time, which would also help avoiding cross-contamination in organic vineyards. Although sulphites were lower in organic than conventional wines, it is not the best indicator to differentiate between both productive methods because the sulphite levels allowed by the EU organic certification are higher enough to not make a difference. Other certifications such as biodynamic and natural wines do make a difference in terms of sulphites, and also organic certifications internationally that do not allow sulphites, as in the United States. Sulphites can become a human health concern in high amounts for particular groups and the population in general, and this should be taken into account by winemakers. Soil residues do point to a difference between both productive methods, as conventional soils were considerably more polluted than their organic counterparts. Beyond lower pesticide content, organic agriculture has the added value of regenerating polluted soils and avoiding future contamination and further pesticide drifts to the environment. At the same time, these results highlight the need to closely monitor the processes of transitioning to organic agriculture in highly polluted soils. The presence of persistent pollutants in the soil decades after their official ban should be an issue of concern, affecting the food chain and the environment as a whole. Harmonised EU soil quality standards and pesticide monitoring policies are long overdue. This study therefore contributes to the research gap on the effects of pesticide application in soils and, in particular, to comparisons between production methods in this area. Further research should also explore more deeply the particularities of pesticide residues in island areas with high application rates and high density agricultural patterns such as the Canary Islands.

CRediT authorship contribution statement

Pablo Alonso González: Conceptualization, Investigation, Writing – original draft, Writing – review & editing. **Eva Parga Dans:** Conceptualization, Data curation, review & editing, Funding acquisition. **Andrea Acosta-Dacal:** Validation, Visualization, Data curation, Writing – review & editing. **Manuel Zumbado Peña:** Validation, Visualization, Data curation, Writing – review & editing. **Octavio Pérez Luzardo:** Conceptualization, Methodology, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2022.104714.

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