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Management of Pesticides from Vineyard to Wines: Focus on Wine Safety and Pesticides Removal by Emerging Technologies

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Abstract

Grapevine (*Vitis vinifera* L.) represent an important crop, being cultivated in 2018 on 7.4 million hectares worldwide, and with a total production of 77.8 million tonnes. Grapes are susceptible to a large number of fungal pests and insects that may cause important economic losses, reduction of quality and undesired sensory characteristics in wines. A common practice in viticulture is the utilization of chemical reagents, as pesticides, that can insure constant production of high-quality grapes. The use of pesticides in vineyards is an old agricultural practice and although generally beneficial, some concerns are raising due to potential toxic compounds assimilation during wine consumption and human health risks. This chapter offers a complete overview of the most common pesticides used in vineyard and tracks them across grapes, winemaking stages and wines. The impacts of pesticide residues on phenolic compounds and volatile compounds are discussed in details, alongside with emerging technologies for removal of pesticide residues from grapes and wines.

Keywords: pesticides residues, winemaking stages, wine quality, pesticides removal technologies

1. Introduction

Grapevine (*Vitis vinifera* L.) represent an important economical and nutritional crop worldwide. Grapes can be consumed as fresh products or processed goods such as wine, jam, jelly, grape seed extract, vinegar, juice, raisins, grape seed oil and pekmez. Grape and wines are among the richest sources of phenolic compounds, including hydroxybenzoic and hydroxycinnamic acids, phenolic alcohols, flavan-3-ol monomers, flavonols, stilbenes, anthocyanins, oligomeric and polymeric procyanidins [1]. In their chemical composition we can find micronutrients, as vitamins B1, B6, C and minerals, as manganese and potassium.

Grapes are known to poses high amounts of carbohydrates and this makes them very vulnerable to damage by diverse fungal pests and insects [2]. High susceptibility to biotic stress of grape varieties can led to important economic loses, reduction

of wine quality and undesirable sensory characteristics. Vines and grapes can be affected by a large number of diseases, such as downy mildew (*Plasmopara viticola*), powdery mildew (*Uncinula necator*), black rot (*Guignardia bidwellii*), Botrytis rot (*Botrytis cinerea*), Eutypa dieback (*Eutypa lata*), Phomopsis cane and leaf spot (*Phomopsis viticola*) and sour rot (*Aspergillus niger*, *Alternaria tenuis*, *Botrytis cinerea*, *Cladosporium herbarum*, *Rhizopus arrhizus*, and *Penicillium spp.*), and many others. The high disease pressure and lack of genetically resistant cultivars have encouraged the use of large amounts of pesticides in vineyards, in order to generate stable yields and high-quality grapes [3]. During the grape production season and later on in winemaking, producers have identified small amounts of pesticides and named them residues. Every year, around 2 million tonnes of different pesticides are used worldwide and it is predicted that the use of pesticides in entire global production will increase up to 3.5 million tonnes [4]. Spraying grapes has to be done multiple times during the vine developmental stages and pesticide residues have been reported in literature by different authors [5].

The use of pesticides in vineyard is a conventional and ancient agricultural practice, which brings many benefits but, unfortunately, some disadvantages as well. Concerns regarding the exposition over a long period of time to pesticide residues present in wines have gained attention in the scientific community. In some cases, inappropriate agricultural practices are used during the application of these active substances in the vineyard. As a result, the amount of pesticide residues on grapes at harvest time exceeds the permitted level by national and international regulations. Alongside with the environmental risks, high amounts of pesticide residues may influence the quality of grapes and wines. Constant consumption of wine or grapes (and indirectly of pesticide residues), can provoke health issues to many consumers. Therefore, it is crucial to monitor the presence of pesticides and regulate their amount in grapes in order to prevent potential health risks. In the European Union, the maximum residue levels (MRLs) of pesticides permitted in products of vegetable origin intended for human consumption is established by Regulation 396/2005/EC [6]. Also, the MRLs limits and the analysis methods are regulated by various international directives [6, 7]. In grapes, the MRLs for pesticide residues often range between 0.01 mg/kg and 5 mg/kg depending on the pesticide, but in some cases higher limits are allowed.

Pesticide residues on grapes may be transferred during winemaking in the juice/must and later to the wine. This means a toxicological risk to consumers despite the fact that winemaking processes (crushing, pressing, fermentation, filtration and stabilization, etc.) can considerably decrease pesticides residues from wines [8]. Each phytosanitary product used in vineyards has a different mode of action which may explain the differences that were observed during analysis. Pesticide residues stability during fermentation and fining stages are factors of concern during winemaking. In red wine production, the maceration-fermentation stage takes place in contact with grape skins, leading to greater residue amounts in raw wine. These types of residues can be adsorbed into solid state during fermentation or filtered out in the fining stages.

Grapes and wines are an indispensable part of people's lifestyle. The world surface devoted to the culture of grapevine is 7.3 million ha, and in Europe is 3.3 million ha [9]. Within the EU, according to the latest available data for 2020, Spain has the topmost area cultivated with vines (961 thousands of hectares-kha), followed by France (797 kha), Italy (719 kha), Portugal (194 kha), Romania (190 kha), Germany (103 kha). World wine consumption in 2020 was estimated at 260 million hectolitres (mhl) and in the EU at 165 mhl. Wine consumption was very high for USA-33.0 mhl, France-24.7 mhl, Germany-19.8 mhl, China-12.4 mhl, Spain-9.6 mhl, Portugal-4.6 mhl, Romania-3.8 mhl, Belgium-2.6 mhl and Switzerland-2.6 mhl [9].

The possible impact of pesticide residues on winemaking stages is a complex subject, and one that has a limited number of literature reports. The influence of pesticide residues on the grapes is a potential source of oenological concerns and can induce wine spoilage and undesired outcomes. The fermentation stage can be disturbed due to the active ingredients of pesticide residues in the must and thus, the quality and structure of wine can be negatively impacted. Pesticide residues can inhibit the yeast activity at the enzyme level and block the cellular metabolic processes of the yeast, leading to problems during the fermentation stage. Pesticide residues impacts on grapes can be influenced by the content of pesticides used in the vineyard, spraying method, spraying time, number of applications and the time difference between last application and harvest.

The morphology, size, and quality requirements of agricultural products are different, thus, influencing the overall content of pesticide residues. In winemaking stages, residues are transferred from the grapes to the wine, in accordance with the physical–chemical properties of their active ingredients, such as vapor pressure, solubility, boiling point, and octanol–water partition coefficient [10]. Processing of grapes using established winemaking techniques can influence the content of residues found in the juice and wine, but it is well established that, in general, wines have lower concentrations than must or grapes [11]. Environmental conditions such as sunlight, temperature and humidity can play a significant role in the kinetic and dynamic behavior of pesticides. In addition, other techniques for reducing pesticides are grape storage and washing processes that can minimize their potential adverse repercussion on human health.

A European Union recent report showed that pesticide residues could be found in more than 86% of grapes; moreover, multiple residues were reported in over 68% of tested samples (in total 2181 table grape samples) [12]. Under these conditions, it is highly recommended to speed up the pesticide residues analysis and come up with reliable, cheap and easy to use methods for identification, quantification and removal of such compounds from grapes, juices and wines.

2. Classification and toxicity of pesticides

Pesticides have a great variety of chemical structures, with diverse action mechanisms and applications. Nowadays, pesticides are presented in a large range of commercially products, with above 800 active components, belonging to more than 100 classes.

Pesticides can be classified bases on the pest type (A) and the origin (B) (**Figure 1**). In the first group of pesticides (A) are included: (1) herbicides, substances used to manage unwanted plant growth or to destroy weeds; (2) insecticides, used to kill infesting insects; (3) fungicides, used to control the propagation of fungi; (4) rodenticides that kill rodents; and (5) nematicides which kill nematodes or adversely affect nematodes. In the second group (B), pesticides can be categorized as chemical (synthetic) and biopesticides (biological or biorationals). The most outspread groups of pesticides are organochlorines, carbamates, pyrethroids and organophosphates. Organochlorines are the first important synthetic organic pesticides that belongs to the class of persistent organic pollutants (POPs). Biopesticides can be separated into two classes, that are, biochemical (hormones, enzymes, pheromones, natural insects, etc.) and microbial (viruses, bacteria, fungi, etc.).

Another classification of pesticides is based on the mode of action or mode of entry. Based on this, pesticides can be differentiated as non systemic, systemic, stomach poison, broad spectrum, disinfectant, nonselective, nerve poison, protectants and repellents. Moreover, pesticides can be classified using their acute toxicity.

Figure 1.
Classification of pesticides.

WHO [13] grouped them in Class Ia = extremely hazardous, Class Ib = highly hazardous, Class II = moderately hazardous, Class III = Slightly hazardous, and Class U=Unlikely to present acute hazards.

Organochlorines (OCs) were among the frequently used pesticides in agriculture, and presented a high toxicity, with hazardous and bio-accumulation properties [14]. These types of pesticides are carcinogenic, persistent in the cycle of environmental degradation, belonging to group of chlorinated hydrocarbons. Moreover, they have high lipophilicity, low polarity and solubility in aqueous medium. OCs are forbidden and no longer used for agriculture in Europe, America and other countries. Organochlorines were substituted with other synthetic compounds such as carbamates, pyrethroids and organophosphorus. These synthetic compounds have a low price, low persistence in nature, high capacity to eliminate a vast number of pests.

The organophosphates and carbamates lead to disturbance in the normal functioning of the central nervous system (CNS), inhibiting the enzyme acetylcholinesterase (AChE) in (CNS) of humans and insects [15]. Organophosphates are widespread contaminants and are correlated with important toxicological threats to the soil, aquatic ecosystems and human health [16].

Pyrethroids are obtained from natural chrysanthemum ester containing natural chemicals, name as pyrethrins [17]. The synthetic pyrethroids have a longer environmental stability and half-life when as compared to the natural form. They have a particular insecticidal activity with reduced toxicity, operation by lagging the voltage gated sodium channel in the neuronal membrane.

Use of such pesticides in modern agriculture is regarded as beneficial for pest control, although residues accumulated in raw products or beverages are extremely dangerous to both human health and the environment. Consumption of wines that may contain residues of pesticides has a strong impact on human health, and may cause muscle weakness, respiratory disorder, paralysis, cancer, etc. [18, 19].

3. Management of pesticides from vineyard to wines

Grape growing and wine production are very complex processes, which start in the vineyard, continue in the winery and end in the consumer's glass. The environmental components, encompassing soil, topography, weather and climate have major impacts on vines growing and grape quality. Management practices in vineyards influence the accumulation of pesticide residues that can potentially affect the final wine chemical composition. Harvesting, transportation and transfer of grapes into the winery and later on the winemaking processes, can modify pesticide residues and gradually reduce or eliminate them.

Pesticide management techniques are constantly changing in accordance with the consumers and policy requirements. The promotion of sustainable viticulture and reduction of chemical inputs in vineyards arises new challenges and concerns for the entire viti-vinicultural sector.

Environmental conditions such as sunlight, temperature, soil, humidity and climate play a significant role in the kinetic and dynamic behavior of pesticides and grapes. Global warming is a key factor that provokes an increase in the accumulation of soluble solids in grapes, in combination with a lower amount of anthocyanins and acidity. As a cascading phenomenon, this slows, or even blocks fermentations and may lead to large economic losses in the winery. In addition, climate change presents a deep effect on the vine phenology, grape composition, winemaking stages, wine chemistry and microbiology and finally on the sensory attributes. Chemical composition of wines, aroma compounds, polyphenolic compounds, color, sensorial characteristics are all affected by the management of vineyards.

Management of vineyard is coordinated by humans and based on their decisions, many components may be affected. Grape quality is dependent on rows orientation, their training system, density, the calendar for pruning, trimming, fungicide treatments, or the way in which soil surface is managed, which comprise its tillage, the manipulation of the canopy structure and nitrogen fertilization [20]. High quality grape berries are influenced by the microclimate, sunlight and water levels. The light influences the evolution of grape volatile compounds, through the amount of light absorbed by the vine leaf area that determines the rate of photosynthesis. All these components generate an uneven distribution of favorable factors that may lead to a high fluctuation of grape quality across different years.

Canopy management includes a series of common techniques, such as the plucking of leaves and head trimming. The first technique improves the microclimate of clusters, provides better fruit maturation, decreasing grapevine diseases incidence [21]. The second one, decrease transpiration and induces the lignification of the plant, balances the growth of branches and insulation within the foliage. Thus, wines resulted from defoliated grapes have higher fruity notes.

In order to obtain a high-quality wine, it is mandatory to have healthy grapes in the winemaking process. Vine growers have to be very careful in the prevention of parasite attacks in vineyards. Phytosanitary treatments used for common vine diseases such as botrytis, powdery mildew or downy mildew may provoke important problems during winemaking. Residues on grapes can be passed to the must and affect the selection and development of yeast strains [8]. Yeast can decrease the pesticides content in the wine. The persistence of pesticides depends on various factors such as the chemical characteristics of active ingredients, photodegradation, thermo-degradation and enzymatic degradation [22].

One of the essential pilons of the horticultural sciences for the control of insect-pests during the second half of XX century is Integrated Pest Management (IPM). There are various strategies to decrease the presence of pesticide residues in wine,

Figure 2. Strategies used to remove pesticides in vineyards. A) Rational use of pesticides in the vineyards. B) Integrated pest management strategies.

such as treatments with sulfur, copper, or plant extracts as alternatives to synthetic products. Another strategy includes scheduled dosages and installation of a meteorological station to relay real-time weather data by General Packet Radio Service (GPRS) connection [23].

In the European Union [24] the use of copper fungicides in organic agriculture is restricted, being limited to 6 kg ha⁻¹ per year [25]. Vallejo et al. [23] found that “weather station” was the most effective to decrease pesticide with wine-growing ecosystem.

IPM is considered as an environmentally friendly approach that can ensure sustainable production, constant yields and high-quality horticultural products [26, 27].

Sustainable agriculture is a key objective of the European Union and a focus of its sustainable development policies. Suitable remedial measures aim to decrease occurrence of pesticides toxicity and other health issues correlated with pesticides. Normally it employs mechanical, cultural and biological methods; allows use of chemical pesticides only when it is required; if possible, bio-pesticide usage, bio-control and indigenous advanced [27]. Some strategies to reduce pesticide residues are presented below and in (Figure 2A and B):

- Rational use of pesticides present advantages that include decreased expenses, decreased environmental impacts and increased safety (Figure 2A) [28].
- Organic strategy is used to increase organic cycles in horticulture, to preserve and improve extended soil fertility, to decrease all types of hazard provoked by pesticides extensive use.
- Awareness of workers: there is an urgent requirement to instruct the farmers and workers regarding the use of pesticides, their toxicity, and the risks of critical pesticide poisoning.
- Sustainable systems can decrease horticultural pesticide using the efficiency–substitution–redesign framework—precision and smart farming, substituting chemical inputs with biocontrol agents or mechanical weed control and improving the current cropping system.
- Genomics and new plant breeding techniques provide huge potential to increase the speed and technical opportunities in the development of resistant

cultivars; plant breeding is a long and complex process, which is often unable to keep pace with the rapid evolution of pathogens or the emergence of new pests — processes that are increasingly driven by globalization and climate change [29].

- Artificial intelligence in agriculture can help identification and classification of weeds, pests and diseases exactly and efficiently; photos taken by drones or from tractor-mounted spraying boots allow targeted spraying and decrease the overall applied pesticide quantities.

4. Effect of pesticides on wine quality

4.1 Pesticides effects on the polyphenolic content and antioxidant activity

A limited number of scientific reports could be found in the literature, regarding the influence of pesticides on the polyphenolic compounds in beverages. In the last years, studies on beer [30–32] and wine [33–35] chemical compositions have been published.

Dugo et al. [33] investigated the phenolic compounds of grapes and wines, after the use of pesticide treatments in the vineyard. Their results indicated that the antioxidant activity of wines was correlated to the content of phenolic compounds. In contrast, each individual phenolic compound was not homogeneous, and the contents were not correlated to various pesticide treatments.

Navarro et al. [30, 31] noticed on beers samples important differences in the total polyphenolic amount after fermentation for samples that contains residues of pesticides. Major reductions were recorded for propiconazole, 70.8%, myclobutanil, 43.0%, fenitrothion, 13.6%, and trifluralin, 6.8%, when compared to the control. Moreover, fenarinol, malathion, methidathion, nuarimol and pendimethalin were not influence by pesticide residues.

In 2011, Navarro et al. [32] observed that not significant differences on the total polyphenolic amount of beer after fermentation with fungicides. In contrast, statistical differences were noticed for the values of color intensity (lower) and tint (higher) in beer.

Recently, Briz-Cid et al. [34] reported that treatment with mepanipyrim decreased 1.2 times the level in monomeric anthocyanin, while polymeric forms increased 1.3 times. Also, after treatment with iprovalicarb the content in the monomeric anthocyanin increased by around 30%. Malvidin derivatives have been affected significantly, increasing up to 42%. Mulero et al. [35] noticed small changes of less than 10%. In his study, quinoxifen and kresoxim-methyl have provoked the biggest increase in total anthocyanin, while the famoxadone, trifloxystrobin and fenhexamid reduced the anthocyanin content. No significant differences in antioxidant activity were observed. Similarly, Mulero et al. [35] reported that presence of pesticide residues did not influence the antioxidant activity in red wines.

In general, the treatment with fungicides did not change very much the concentrations of monomeric anthocyanins or flavan-3-ol monomers in wine [36]. Exceptions have been reported for treatments with boscalid + kresoxim-methyl which increased the amount of flavonoid groups with 58% and 36%, respectively. Mulero et al. [35] presented similar results for Monastrell wines from grapes treated with kresoxim-methyl. The treatment with quinoxifen indicates an increase of phenolic compounds in wines when compared with control sample. In opposite, when trifloxystrobin was used it was observed a lower total content in phenolic compounds.

Castro-Sobrino et al. [37] indicated that the use of pesticides does not have an effect on anthocyanins. However, tetraconazole use led to a decrease of these compounds.

4.2 Pesticides effects on the aromatic profile

Wines represent a very complex matrix that contains hundreds of volatile aroma compounds. Aroma compounds originate from: i) varietal aroma that come from the vine and is released in the wine during the fermentation process. The most powerful varietal aromas are terpenoids, varietal thiols and methoxypyrazines; ii) fermentative aroma as a result of the synthesis of important volatile compounds through *Saccharomyces* and non-*Saccharomyces* yeast metabolism, are mainly constituted of volatile higher alcohols, acetate and ethyl esters, medium- and long- chain volatile acids, aldehydes, sulfur compounds [38]; iii) aging aroma either in bottles, in oak barrels or with oak chips, staves with the accumulation of characteristic new aroma compounds (**Table 1**).

Wine aroma can vary depending on the geographic area and terroir, viticultural practices, winemaking processes, type of aging and bottling. Moreover, other factors that have impact on the aroma compounds can interact with proteins, oxygen, polyphenols, polysaccharides, and thus modifying the sensorial characteristics of wines. A correct and controlled management of various methods or conditions of winemaking can help improve wine quality thorough removing the unwanted aroma compounds, the residues of pesticides or heavy metals, microbial contamination or oxidation, etc.

C6-alcohols belong to the group of C6-compounds and are formed during pre-fermentation stages, especially during harvesting, transport, crushing and pressing of grapes. These compounds are principally related to lipoxygenase activity in grapes or in must which produces aldehydes, then these, in turn, can be reduced to alcohols, by yeasts during fermentation stage. Higher alcohols are formed from their amino acid precursors, then are passed on to the wine, which are liable for fermentative aroma.

Reports suggested that the residual content of cyazofamid, famoxadone, mandipropamid and valifenalate was not affected by the synthesis of alcohols [47]. Similar results were published by other authors, regarding the chlorpyrifos, fenarimol, mancozeb, metalaxyl, penconazole, vinclozolin, fluquinconazole, kresoxim-methyl, quinoxifen and trifloxystrobin in red wines [48] and with fludioxonil and pyrimethanil in white wines [49]. Interesting, opposite impacts were noticed for other pesticide categories. In red wines, a significant decrease of alcohols was observed when famoxadone, fenhexamid and tebuconazole were used [39, 48]. Contrasting, in white wines an increase of cis-3-hexen-1-ol content was observed in the presence of cyprodinil [49]. The same trend was noticed for tetraconazole in wines, in which the levels of cis-3-hexen-1-ol also increased with 55% [40].

A pesticides treatment that included fluxilazole showed that, in white wines, the content of isoamyl alcohols and 2-phenylethanol was increased with a direct correlation to the dose [50]. Moreover, other studies observed in white wines a decrease of 2-methyl-1-propanol and 3-methyl-1-propanol when fosetyl-A, mancozeb and iprovalicarb were used [41]. Results concerning the decrease of alcohols concentrations in the presence of some pesticides can be attributed to lower assimilation of the amino acid precursor by yeast or modifications in the biosynthesis of amino acids. However, a decrease in the quality of wine was noticed due to considerable increases in isoamyl alcohols contents [48, 49]. González-Álvarez et al. [47]

Pesticides	Pesticides losses	Quality and health risks of wine	Ref.
Iprovalicarb Mepanipyrim Tetraconazole	The fungicides mepanipyrim and tetraconazole exhibited a high dissipation rate during the winemaking process (93–98%); about 10–18% of iprovalicarb remained in wine.	The total content in the monomeric anthocyanin of iprovalicarb treatment increased by about 30%. Fungicides in wine do not only poses a health risk but also can alter fermentation and hence the quality of the wine	[34]
Metrafenone Boscalid + kresoxim-methyl Fenhexamid Mepanipyrim	no data	Presence of boscalid + kresoxim-methyl residues in must impairs the sensory quality of the resulting wine by diminishing its brightness and aroma. It increased the contents in monomeric anthocyanins (58%) and flavan-3-ols (36%), and also color lightness (20%), but decreased the contribution of the ripe (42%) and fresh fruits (59%) odorant series.	[35]
Fenhexamid Kresoxim-methyl Fluquinconazole Famoxadon Trifloxystrobin Quinoxifen	no data	Wines from grapes treated with quinoxifen shows an increase of phenolic compounds than the control. In contrast, the wine obtained from grapes treated with trifloxystrobin showed lower total concentration of phenolic compounds.	[36]
Mepanipyrim (Mep) Tetraconazole (Tetra)	no data	No effects on anthocyanins for mepanipyrim treatments were observed. A decrease of these pigments was registered when Tetra and Tetra-Form were applied; moreover Tetra-Form reduced phenolic compounds.	[37]
Tebuconazole	no data	The presence of residual levels of tebuconazole had no effect on varietal aroma compounds, terpene and higher-alcohol concentrations were essentially not changed; by contrast, C6-alcohol, ester and aldehyde concentrations differed significantly.	[39]
Mepanipyrim Tetraconazole	no data	Mep residues affected the release of varietal aroma compounds from their grape precursors, Tetra residues mainly affected the aroma biosynthesis pathways of the ethanol producing yeasts. Presence of Mep residues in grape must could contribute to wines having higher “floral” and “spicy” notes and lower “fruity” nuances while the presence of Tetra residues can contribute to wines having higher “floral and lactic” nuances.	[40]

Pesticides	Pesticides losses	Quality and health risks of wine	Ref.
Benalaxyl, Iprovalicarb, Pyraclostrobin	no data	Reduced the varietal aroma of wines attributed to geraniol. Increase in the fruity aroma due to several ethyl esters and acetates	[41]
Quinoxifen	79–82% fungicide removal by alcoholic fermentation.	Quinoxifen led to significantly lower ethylic ester levels. The addition of the fungicide did not seriously inhibit biomass production. A slight decrease of ethanol production in terms of both absolute value and conversion yield of ethanol produced per sugar consumed was, however, observed when the quinoxifen concentration was increased.	[42]
Fenamidone, Pyraclostrobin, Trifloxystrobin	After winemaking, fenamidone, pyraclostrobin, and trifloxystrobin were not detected in the wine, but they were present in the cake and lees.	These three active ingredients could be used in a planning to obtain residue-free wines.	[43]
Iprovalicarb, Indoxacarb, Boscalid	Winemaking showed a complete transfer of all pesticide from grapes to the must, while in wine the residues were negligible due to the adsorbing effect of lees and pomace.	No risks of quality and safety defects.	[44]
Cyprodinil, Fludioxonil, Pyrimethanil, Quinoxifen	Fludioxonil decreased most quickly during winemaking without maceration, whereas the decrease of pyrimethanil was the slowest in all cases. During carbonic maceration winemaking, the decay constant of cyprodinil was greater than that of the other pesticides.	The winemaker can also choose which winemaking process to follow depending on the residues.	[45]
Carbendazim, Chlorothalonil, Fenarimol, Metalaxyl, Procymidone, Triadimenol Carbaryl, Chlorpyrifos, Dicofol	After malolactic fermentation the concentrations of the active compounds chlorpyrifos (70%) and dicofol (30–40%) were the most significantly reduced.	In the case of dicofol, a substantial slowing of malolactic fermentation was observed when this compound was present at high concentration. Dicofol had a major inhibitory effect on the catabolism of malic acid (6–13% was metabolized), whereas chlorothalonil, chlorpyrifos, and fenarimol had only a minor effect (76–84% was metabolized).	[46]

Table 1.
Pesticides losses, quality and health risks of wine.

reported no significant differences in the alcohols level between control sample and wines treated with chlorpyrifos, cyazofamid, famoxadone, fenarimol, mancozeb, mandipropamid, metalaxyl, penconazole, valifenalate and vinclozolin.

The level of aldehydes increased slowly in the wine aging stage by effect of the oxidation of alcohols. The principal aldehydes that could be found in wines are benzaldehyde and phenylethanal [51]. Until now, results indicate that pesticides utilization do not influence the aldehyde contents [39]. However, in red wine, fenhexamid seems to be responsible for the increased content of benzaldehyde [48].

Sieiro-Sampedro et al. [40] founded that mepanipyrim influence the release of varietal aroma compounds while tetraconazole have a major impact on the aroma biosynthesis pathways of the ethanol producing yeasts. According to the OAV, the mepanipyrim could offer to wines higher spicy and floral nuances and lower fruity note whereas tetraconazole leads to higher floral and lactic notes. Mepanipyrim (Mepp) and Mep-Form generated a positive increase of the geraniol content, between 27 and 41%, benzyl alcohol between 91 and 177%, benzaldehyde between 51 and 111% and *trans*-isoeugenol between 37 and 308%. This trend was associated with the actions of yeast enzymes glycosidase and hydrolase of which activity is known to increase during fermentation.

Esters are produced by yeast during the alcoholic fermentation and play an important role in the fruitiness of wines.

The effect of cyprodinil, fludioxonil and pyrimethanil presented lower levels of hexanoate, ethyl octanoate and ethyl decanoate in white wines [49]. Also, grapes treated with quinoxifen, kresoxim-methyl and trifloxystrobin have decreased the content of ethyl dodecanoate and diethyl succinate in wines [41]. García et al. [49] observed an increased content of isoamyl acetate in the presence of cyprodinil, fludioxonil, chlorpyrifos, feranimol and vinclozolin. The level of ethyl acetate increased also when chlorpyrifos were used, whereas decreased its content with famoxadone and fenhexamid [48]. Other studies did not notice differences in ethyl ester and acetate levels in control sample and grapes treated with cyazofamid, famoxadone, mandipropamid and valifenalate [47]. Similarly, Noguerol-Pato [39] reported no significant variations, caused by treatments with tebuconazole, in the level of isopentyl acetate and most ethyl esters found in Mencía wines. On the other hand, residues of other pesticides seemed to increase the content of isopentyl acetate [41, 48].

Terpenes are found in grape skin, have an important role in varietal aroma and contribute considerably to the grape bouquet.

Oliva et al. [48] reported that treatment with some pesticides (famoxadone, fenhexamid, fluquinconazole, kresoxim-methyl, quinoxifen and trifloxystrobin) presented an increase of terpenoic class in red wine comparative with control sample. Another study by González-Álvarez et al. [47] showed that cyazofamid and famoxadone treatments have a major impact in the synthesis of *trans*, *trans*-farnesol of white wines. Also, three fungicides (benalaxyl, iprovalicarb and pyraclostrobin) have altered the geraniol synthesis [41]. On the contrary, Noguerol-Pato et al. [39] observed that tebuconazole caused no important changes in the terpenoic content of red wines.

The treatment with famoxadone and cymoxanil led to a reduction in the content of isovaleric, caproic and caprylic acids, while valifenalate and cyazofamid increased the content of capric acid, according to González-Álvarez et al. [47]. In another study, the quinoxifen, kresoxim-methyl, famoxadone, trifloxystrobin, fluquinconazole and fenhexamid content decreased the acid concentration in red wines compared with control sample [48].

Lactones are obtained through the intermolecular esterification of 4- hydroxy-acids. The use of pesticides on crushed Tempranillo and Graciano grapes did not affect the formation of lactones.

5. Emerging technologies to remove pesticides from grapes and wines

Pesticide residues in grapes and by-products can be a major concern to human health. The majority of grape products are consumed raw or slightly processed [52]. It is imperative to identify processes that are able to decrease and remove the pesticide residues from all horticultural products.

Certain processes, like washing [53], peeling [54], or cooking [55] have been reported in literature as good methods to decrease the content of pesticide residues and also reduce the risk of exposure to these phytosanitary products. However, some horticultural crops such as grapes are not subjected to a washing stage in their industrial processing line, and they are not peeled or cooked previous to consumption. Commonly, grapes are treated followed a phytosanitary scheme in the vineyard, harvested and then directly subjected to the winemaking process.

Proactive removal of pesticide residues from grapes and wines can be done by using decontamination techniques, classified as physical, physical–chemical and oenological methods (Figure 3). Apart from the classic methods used for reducing pesticide residues, the application of new or emergent technologies such as pulsed electric field (PEF) or ultrasounds, in the grapes and wines, is a current research hotspot.

5.1 Physical methods

Physical methods partially eliminate pesticide residues from grapes and wines are used on a small scale in the wine industry. Most of these techniques are not economically feasible for most small to medium size winemakers, even if nowadays, the modern beverage processing technologies aim at beverages safety and sustainable production.

Figure 3. Removal of pesticides from grapes and wines.

Pulsed electric field (PEF) method is an emergent non-thermal technology that induces a lower degradation of compositional and sensorial characteristics than the classical thermal processing. This method uses an electric field in the form of short or high voltage pulses. The beverage is placed into the electric field, between two electrodes for a short period, regularly in the microsecond scale [56].

Zhang et al. [57] reported that PEF method in apple juice can reduce the content of diazinon and dimethoate. The efficacy of PEF can be improved with increased process time and the strength of the electric field. Efficient removal of diazinon (47.6%) and dimethoate (34.7%) was realized when using 20 kV cm⁻¹ for 260 μs.

Delsart et al. [58] studied the impact of the same treatment on vinclozolin, pyrimethanil, procymidone, and cyprodinil in wine samples. Results revealed that PEF method can decrease the fungicide content and the major factors of influence were the electrical field strength and used energy level.

Ultrasonics represent a promising innovative and green method, which offers numerous advantages, such as simplicity, cheap, energy-saving. The principal limitations of this technique and its wide use in the industry can be solved by combining it with other compounds or treatments.

Ultrasonic dishwasher is a recent technique used in elimination pesticides from fruits and vegetables [59]. Ultrasonic waves provoke a phenomenon such as cavitations, which leads to the fast formation and violent collapse of micron-sized bubbles in a liquid medium. This method with tiny implosions that ensure the cleaning power, using the ultrasonic washing, was not exploited to its maximum potential. In a recent study, Zhou et al. [60] investigated the ultrasonic washing process to eliminate pesticides from grapes. Washing with the ultrasonic dishwasher proved to be more efficient for pesticides removal. Results showed residues decreased rates between 72.1% and 100% on grapes when comparing with normal water washing.

Another very promising emerging technology used for grape products is **micro-filtration**. This method uses a membrane technology driven by pressure and, up to date has found many practical applications for pesticides reductions, offering several technological advantages [61]. Among the advantage of microfiltration are the high separation efficiency, low energy consumption, easy implementation and operation, absence of phase transition and non-use of additional solvents, which favor the solute recovery. Doulia et al. [62] investigated microfiltration in process of elimination of pesticides from a Greek wine, utilizing six membranes with the same pore size 0.45 μm. The membranes used were: cellulose acetate (CA), cellulose nitrate (CN), regenerated cellulose (RC), polyethersulfone (PESU), polyamide (PA) and nylon (NY). Results on the effectiveness of pesticides removal were as follows for white wine: cellulose acetate > cellulose nitrate > polyethersulfone > nylon > regenerated cellulose > polyamide and for red wine: cellulose acetate > cellulose nitrate > regenerated cellulose > polyethersulfone > polyamide > nylon. Another aspect found by the authors was that the bigger hydrophobicity and the lower hydrophilicity of pesticide, the higher the microfiltration effectiveness for both wines. Moreover, Doulia et al. [62] showed that the hydrophobic pesticide removal is more effective in red wines than in white wines, for all six membranes. This seems to be caused by the presence of higher amounts of hydrophobic polyphenolic compounds in red wine.

5.2 Physical: chemical methods

One of the known methods for pesticides removal is the chemical adsorption. This method is described as eco-friendly, low production of by-product waste and cost-effectiveness. Various types of adsorbents such as clay, activated carbon,

biochar and nanoparticles have been used for the adsorption of pesticides from grapes and wines. Adsorption techniques can be chemical, as bonding through ion-dipole interactions, weak Van Der Waals, forces, dipole–dipole, cation exchange and strong covalent bonding or physical adsorption [63]. Effective removal of pesticide residues depends on the pesticides concentrations, the wine fining agents, the type of compounds and the dosage.

Ozone (O₃) treatment is a new modern technique with various uses in food and beverage industry like as pesticide removal, water remediation and decontamination of fresh fruits. Ozone has been accepted by the World Health Organization (WHO), Food and Drug Administration (FDA) and by the Food and Agriculture Organization of the United Nations (FAO) for usage as an antimicrobial agent for the treatment, storage and processing of foods in gas and aqueous phases in 1997 [64]. Since that time the ozone treatment has been utilized in the agri-food-beverage sectors, in particular to control postharvest decay and extend shelf-life of fruits and vegetables [65]. It was shown that postharvest ozone treatments improve resveratrol and other phenolic compounds [66] and decrease pesticide residues [67].

Ozone can be used in various forms such as dry, watery and moist during the decontamination method. O₃ in the beverage processes is used as an oxidant for pesticide content reduction. The percentage of pesticide removal depends on the ozone characteristics and not only on the chemical pesticides composition. Thus, it is obvious that specific conditions are necessary for the effectiveness of the ozonation process. The elimination of pesticides is influenced by different conditions of application (pH, temperature and humidity), organic matter content, ozone concentration, production rate and form of application (aqueous and gaseous) [68].

The principle of this technique consists of ozone generation by the passage of air, or oxygen gas through a high-voltage electrical discharge or by ultraviolet light irradiation [69]. The product of ozone degradation is oxygen; thus, it leaves no residues on treated items. There are other possible benefits of ozone, like the elimination of mycotoxins [65], pesticide residues and microbiological control of food products [70].

In 2015, Dordevic and Durovic-Pejcev [71] affirmed that juice processing may eliminate the pesticide amounts by using washing/cleaning, pulp-removing, pressing, squeezing, clarification (like centrifugation, enzymatic treatment and filtering) and heat treatment (like boiling, pasteurization and sterilization). Botondi et al. [72] suggested to utilize ozone fumigation postharvest, in order to analyze microorganisms and evaluate the influence on polyphenols, anthocyanins and cell wall enzymes during the grape dehydration for wine production. Ozone treatments decreased yeasts and fungi by 50%. Moreover, a treatment that used shock ozone fumigation before dehydration decreased the microbial count during dehydration without influencing the polyphenol and carotenoid amounts. In 2018, Karaca [73] studied the removal of pesticides from grapes by exposing fruits in ozone-enriched air. Gaseous ozone rich atmosphere led to a 2.8-fold higher removal of azoxystrobin fungicide than control sample. Both phases, gaseous and aqueous ozone techniques displayed 67.4% and 78.9% decrease of chlorothalonil residues from table grapes [74]. The differences in the efficacy of pesticide residues may be assigned to the diversity in the structure of the pesticides.

Activated carbon (AC), is generally used in winemaking to remove phenolic compounds, pigments and off-flavors. AC has high and broad affinities especially for benzoid and non-polar substances. Activated carbon shows large positive effects on reduction of pesticides, due to its high adsorption capacity, large surface area and high porosity.

Sen et al. [75] studied the influences of activated carbon with low, middle, high doses on the removal of vinclozolin, penconazole, endosulfan, imazalil, nuarimol

and tetradifon used in viticulture. The amount of imazalil decreased in white wine with middle and high doses of activated carbon, but low dose of activated carbon removed 92.96% of imazalil. This result can be associated to the high adsorption surface of carbon and to the limited interference from the wine chemical compounds.

Nicolini et al. [76] investigated whether small amount of pesticide residues can be removed adding a low dose of activated carbon during fermentation. AC decreased up to 130 µg/L of fungicides in the white wine samples studied. Results obtained in wines fermented with activated carbon had 30–80% lower fungicides as compared to the control. An exception was found in the case of iprovalicarb which did not significantly decreased.

Bentonite is a natural montmorillonite clay and in nature has Mg^{++} , Ca^{++} , Na^{+} , aluminum and silicon oxide forms. The most used form of bentonite in wine-making is sodium bentonite, which has a large adsorption surface. This surface has a strong negative charge, and it allows ion exchanges and other electrostatic interactions. Bentonite sodium is used largely in winemaking for the elimination of positively charged proteins. Among the disadvantages of bentonite are the non-selective elimination process and the reduction of valuable aroma compounds from wines [77, 78].

Sen et al. [75] reported that bentonite had a major effect on decreasing the concentrations of imazalil (96–98%), endosulfan (81–87%), and penconazole (84–95%). However, bentonite influence on nuarimol and tetradifon was limited, removing between 15 and 33% and 25–39%, respectively. Bentonite had no influence on the elimination of vinclozolin. Ruediger et al. [79] has shown that 500 and 2500 mg/l of bentonite eliminated a large amount of pesticides from white wines. The authors have found that there was not a clear effect of an increased dose of bentonite on triadimenol and metalaxyl.

Navarro et al. [80] showed that filtration of wines, previously clarified with bentonite and gelatin, lead to the removal of 2% metalaxyl, 7% fenarimol, 25% penconazole and 28% vinclozolin. During maceration stage, the rate remaining of chlorpyrifos, penconazole and metalaxyl was 90%, while the percentage of fenarimol, vinclozolin and mancozeb was lower (74–67%).

Likas et al. [81] reported that processing of treated grapes into wine almost removed residues for flufenoxuron and lufenuron resulting in residue-free wine, whereas tebufenozide was found in wine at concentrations from 0.13 to 0.26 mg/L. Among the fining agents used, bentonite, potassium caseinate, gelatine–silicon dioxide and polyvinylpyrrolidone did not actually eliminate residues from wine, while charcoal very effectively removed tebufenozide residues. The pesticide residues in grapes presented a low removal for 42 days after phytosanitary treatment, with dissipation rates varying from 0.011 to 0.018 mg/kg day. The pesticide residues have shown for 0.27 mg/kg for flufenoxuron, lufenuron and 0.68 mg/kg for tebufenozide, and their concentrations were lower than the maximum residue limits (MRLs).

Chitosan is a biopolymer obtained from chitin and comprises N-acetylglucosamine and glucosamine units. These properties of the chitosan structure give its flexibility and heterogeneity. Hydrophilic functional groups cannot alter chitosan's hydrophobic nature and support adsorption [82].

Venkatachalapathy et al. [83] studied the pesticide removal efficacy, when using chitosan fining agent in grape juice during the clarification stage. In this study, pesticide removal efficiency of chitosan ranged from 54–72% at 0.05% chitosan concentration, and increased up to 86–98%, when higher chitosan concentration was used (up to 0.5%). Results showed that 0.05% chitosan had the highest pesticide removal efficiency (72%), when compared other clarifiers. Also, investigations showed that

the optimal pesticide elimination was achieved using chlorpyrifos (98%) and ethion (97%) at chitosan for 1 h incubation continued by phorate (96%), fenthion (95%), fenitrothion (94%) and diazinon (86%) at chitosan for 2 h incubation time.

In recent years, a new carbon rich adsorbent (38–80%), **biochar**, attracted remarkable attention. Biochar is produced by thermal conversion under oxygen free environment [84]. Yuan et al. [84] expressed that the biochar surface brings negative charges because of the occurrence of organic groups. Biochar can be used for the elimination of different toxic compounds such as pesticides, heavy metals, antibiotics and dyes. Biochar has unique characteristics such as higher pore volume, larger surface area, high environmental stability, low cost and extensive raw material sources [85]. Moreover, other materials like clay, zeolite, mesoporous materials were also used for the removal of pesticides from grapes and wines.

Grape pomace (GP) is a by-product of various grape based manufacturing processes, such as juice, jam-making, wines, etc. The GP biomass represents around 20–30% of the residual biomass of grapes. European countries reported GP wastes of about 1,200 tons per year. Yoon et al. [86] investigates in his work the adsorptive comportment and mechanisms of grape pomace-derived biochar (GP-BC). Pesticide cymoxanil removal rates were assessed during this study. Biochar produced at 350°C achieved the maximum adsorption capacity of 161 mg CM/g BC at pH 7 for cymoxanil. Thus, cymoxanil adsorption was attributed to the combined influences of metal and hydrophilic interaction.

Angioni et al. [44] has researched the transfer from grapes to wines during the entire winemaking process for some pesticides. The concentrations found in grapes were under limits set by the EU, having the amounts 0.81, 0.43, and 4.23 mg/kg for iprovalicarb, indoxacarb, and boscalid, respectively. The obtained results showed that all pesticides have been transferred from grapes to the must, whereas in wines the residues were insignificant. For pesticides, the clarification stage presented a good elimination of these toxic compounds from wines.

5.3 Oenological techniques

Winemaking processes have the potential to remove, degrade or decrease pesticides content in grapes. This is achieved mainly through stages of winemaking, such as pressing, filtration, adsorption or through microbial processes occurring during the fermentation stage [87, 88].

In the first stages of winemaking, in pressing and maceration process, the pesticide residues on grapes are decreased notably. Thus, a considerable amount of toxic compounds remain in the cake and lees, and a small quantity migrates into the must [89]. In the next stage, in alcoholic and malolactic fermentation, yeasts destroy some part of pesticide residues. Another important stage in which takes place the reduction of pesticide residues is the clarification step [90].

Pan et al. [91] found that the whole process can reduce the zoxamide residue in red and white wines. Peeling process has an important influence on the decrease of zoxamide, because a high content of this pesticide was retained by the grape skin. These results can provide more accurate risk assessments of zoxamide during winemaking process. Pazzirota et al. [92] found that pesticide distributions over the different stages of winemaking process were clearly dependent on the affinities of pesticides to organic or aqueous fractions in the process. The pesticide contents decreased from grape to wine. Decreases from fermentation stage during maceration are due to pesticide affinities for solid residues present in the sample for cyprodinil and imazalil.

Yeast have the ability to decrease pesticide residues from wines, by degradation and/or adsorption. The removal of pesticides during winemaking has been widely studied [93]. In this process, the main agent for adsorption is the yeast cell wall,

containing polysaccharides as basic building blocks. It has been shown that the principal fraction of mannoproteins is released in the first week after the alcoholic fermentation has finished. In this stage the dominant adsorptive action is noticed. Also, at the end of the alcoholic fermentation, *bâtonnage* is used to obtain higher quality wines. The mannoproteins are released and the adsorption of pesticides take place [94]. However, not only strain properties, but also differences in the binding affinity of pesticides, are important factors. The adsorption of yeast lees is different among strains, and due to the cell wall structure, physicochemical conditions, especially pH, influence the adsorption ratio [94].

Elimination of pesticides by degradation is an uncommon process. Yeast have the ability to degrade some pesticides from the pyrethroid class and insecticides thiophosphates class [95]. During fermentation, yeasts partially degraded quinoxifen and adsorbed it completely [89]. It has been shown by Cabras et al. [89] that fenhexamid did not affect alcoholic fermentation, whereas a great content of pyrimethanil (10 mg/L) was found to significantly diminish the anaerobic growth of *Hanseniaspora uvarum* [96]. In other studies, the presence of pesticides has been found to stimulate yeasts, especially *Kloeckera apiculata*, which produced more alcohol [97]. Oliva et al. [98] found that no fungicides delays or inhibits fermentation processes. Also, the evolution of yeast populations during fermentation follows the normal multiplication processes of the species.

6. Conclusions

Increased population, higher demand from quality beverages, rapid climatic changes and the need for more phytosanitary treatments constitute to a wine industry that has to focus more on sustainable practices, high grape yields and minimized health risks. Conservator winemakers that use adequate agricultural practices can limit potential negative effects that are linked to higher pesticide concentration in wines. However, the high pressure of climatic conditions, increased pathogen virulence and mutations into new variants can increase the quantities of pesticides needed in vineyards and led to potential human health risks. Large pesticide quantities may affect negatively the water and soil quality, leading to undesired effects on the animals, plants and human communities.

Different techniques have been used successfully to remove pesticide residues from grapes and wines. Technologies such as pulsed electric field (PEF), ultrasounds (US), microfiltration, ozone (O₃), adsorbents used during pressing, fermentation and filtration are nowadays implemented by many winemakers. However, preventive methods applied directly from vineyards and emergent technologies should be utilized to produce grapes with tiny amounts of pesticides. Effective pesticide management requires actions supported by a very clear and transparent legal system and toxicity regulations.

Integrated pest management strategies could provide a more efficient control of pesticides use and limit the residues. Utilization of precision spraying and local treatments can reduce the pesticide residues negative impact on the environment and potential human health risks.

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