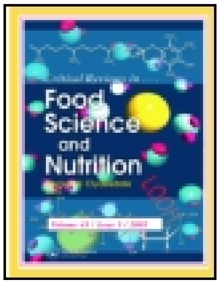

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A Review on the Fermentation of Foods and the Residues of Pesticides — Biotransformation of Pesticides and Effects on Fermentation and Food Quality

Jorge Regueiro [a], Olalla López-Fernández [a], Raquel Rial-Otero [a], Beatriz Cancho-Grande [a] & Jesús Simal-Gándara [a]

[a] Nutrition and Bromatology Group, Department of Analytical and Food Chemistry; Food Science and Technology Faculty , University of Vigo – Ourense Campus , E-32004 , Ourense , SPAIN

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Jorge Regueiro, Olalla López-Fernández, Raquel Rial-Otero, Beatriz Cancho-Grande, Jesús Simal-Gándara*

Nutrition and Bromatology Group, Department of Analytical and Food Chemistry; Food Science and Technology Faculty, University of Vigo – Ourense Campus, E-32004 Ourense, SPAIN.

* Corresponding author (jsimal@uvigo.es)

Tel.: +34 988 387000

Fax: +34 988 387001

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Abstract

Residues of pesticides in food are influenced by processing such as fermentation. Reviewing the extensive literature showed that in most cases this step leads to large reductions in original residue levels in the fermented food, with the formation of new pesticide by-products. The behavior of residues in fermentation can be rationalized in terms of the physical-chemical properties of the pesticide and the nature of the process. In addition, the presence of pesticides decrease the growth rate of fermentative microbiota (yeasts and bacterias), which provokes stuck and sluggish fermentations. These changes have in consequence repercussions on several aspects of food sensory quality (physical-chemical properties, polyphenolic content and aromatic profile) of fermented food. The main aim of this review is to deal with all these topics to propose challenging needs in science-based quality management of pesticides residues in food.

Keywords: pesticides; fermented food; sensory quality losses; metabolites

Glossary

CAP	Critical agricultural practices
CHB	7-Chloro-6-hydroxy-2-(1-methylcyclohexyl)-1,3-benzoxazole
DDD	1-Chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene
DDE	1,1-Dichloro-2,2bis(p-chlorophenyl)ethylene
DDT	1,1,1-Tricloro-2,2-bis(4-clorofenil)-ethane
EBDC	Ethylene bisdithiocarbamate
EFSA	European Food Safety Authority
ETU	Ethylenethiourea
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
GAP	Good Agricultural Practice
H.	*Hanseniaspora*
HCB	Hexachlorocyclobenzene
HCH	Hexachlorocyclohexane
IUPAC	International Union of Pure and Applied Chemistry
JMPR	Joint FAOWHO meeting on pesticide residues
K.	*Kloeckera*
Kow	Water–octanol partition coefficient
L.	*Lactobacillus*
LAB	Lactic acid bacteria
MRLs	Maximum Residue Limits
O.	*Oenococcus*
OHA	Hydroxyatrazine
OHT	Hydroxyterbutylazine
OPPs	Organophosphate pesticides
PBDC	Propylene bisdithiocarbamate
PDP	Pesticide Data Program
PTU	Propylenethiourea
S.	*Saccharomyces*
St.	*Streptococcus*
THPI	Tetrahydrophthalimide
US	United States

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USDA	United States Department of Agriculture
var.	Variety
WHO	World Health Organization

1. Residues of pesticides in foods

The current model of agriculture is designed to maximize profit by increasing production yields and quality of agricultural products, while reducing costs for both producers and consumers. In this regard, the use of pesticides has paid an enormous importance allowing controlling insect or fungal infestations or growth of weeds, either to handle immediate infestations or to anticipate long-lasting problems (González-Rodríguez et al., 2011c). Pesticides can also be used to help protect seeds, or prolong the life of crops after they have been harvested.

However, despite their many merits and due to their inherent nature, pesticides are some of the most toxic, environmentally stable and mobile substances in the environment. Their excessive use/misuse especially in the developing countries, their volatility, long-distance transports eventually results in widespread environmental contamination (Kaushik et al., 2009). In addition, many older, non-patented, more toxic, environmentally persistent and inexpensive chemicals are used extensively in developing nations, creating serious acute health problems and local and global environmental impacts (Ecobichon, 2001). As a consequence of their extensive applications, most of the applied pesticides find their way as 'residue' in the environment into the terrestrial and aquatic food chains, where they undergo concentration and exert potential, long term, adverse health effects (Kaushik et al., 2009). Nevertheless, the perception on the risks that pesticide residues in food pose to human health relative to other dietary risks varies between consumers and scientists. One cause of this misconception has been the emphasis placed on "worst case" evaluations and extrapolations of available data e.g. assuming that all crops are treated with pesticides and that the resulting residues in food as consumed are at maximum permitted levels (Holland et al, 1994). **Table 1** (Thundiyil et al, 2008) gives examples of pesticide classes and clinical presentations of possible adverse health effects resulting from unsafe exposure. The severity and likelihood of effects from acute pesticide poisoning can vary according to a specific agent, dose, underlying physiologic reserve, co-morbidities, route of exposure, organ system, age, poverty (Tinoco-Ojanguren and Halperin, 1998; Mancini et al., 2005), education (Oliveira-Silva et al., 2001) and other factors.

Each year, 140,000 tons of pesticides are sprayed onto crops in the European Union (EU) alone. Pesticides slowly start dissipating after these are sprayed. The rate at which pesticides are moved or dissipated varies with the nature of pesticide molecule, type and portion of food material and environmental factors (Bajwa and Sandhu, 2011). Every pesticide used on crops needs some waiting period before harvesting that differs from pesticide to pesticide and also from one crop to another. If the conditions of good agricultural practice (GAP) such as applicable doses of the pesticide and the time interval between applying the pesticide and harvesting the crop are not met, harvested crops may contain unacceptable levels of pesticide residues (González-Rodríguez et al., 2011c). Fruit and vegetables are the crops most likely to be contaminated by pesticides, particularly grapes, citrus fruits and potatoes (Fenik et al., 2011). According to the EU's Pesticide Action Network, 138 pesticides had to be analyzed in 2009 in 300 different samples of plant and animal origin (EFSA, 2011). The analysis of the results has shown that 1.2% of the samples exceeded the maximum residue limits (MRLs), generally used to control the pesticide residues on crops; 37.4% of samples had measurable residues above the analytical reporting level but below or at the MRL and 61.4% of the samples were free of measurable pesticide residues. The pesticide/crop combinations where residue values were measured most frequently were imazalil/bananas (49.5%), chlormequat/wheat (42.3%) and fenhexamid/table grapes (23.8%).

While MRLs are useful to monitor the correct use of pesticides, they are inadequate to monitor the risk to human health from pesticide residues since the total diet studies have shown an over-estimation of the actual intakes by one to three orders of magnitude (WHO, 1989; Winter, 1992). In this sense, the International Union of Pure and Applied Chemistry (IUPAC) has recommended a stepwise approach to evaluating risks from pesticide residues in food which includes allowance for losses in processing (Bates and Gorbach, 1987). As a result of the processing studies, it is possible to recognize reductions and concentrations of the residues and to calculate processing factors for important products. Such studies have been found to be critical for better estimates of dietary intake of pesticides. They are also useful in identifying the pesticides with maximum degradative potential/dissipation behavior during such processing method and least harmful to the yeast growth for better management of residues in such products.

In this regard, it was demonstrated that processing treatments such as washing or cleaning, peeling, blanching, juicing, cooking, milling, baking, pasteurization, canning, etc., can often substantially reduce the residue levels on or in food that has been treated with pesticides (Wen et al., 1985; Abou-Arab, 1999a; Soliman, 2001; Sharma et al., 2005). However, in some special cases more toxic by-products or metabolites can be formed during processing and also residues level can increase due to concentration effect and/or affinity for lipid moiety (Holland et al., 1994; Bajwa and Sandhu, 2011). From an effective point of view, food safety monitoring programs must consider all these possible situations. Therefore, the results of the processing studies should be used as follows:

- to provide information on the transfer of residues from the raw agricultural commodity to the processed products, in order to calculate reduction or concentration factors;
- to enable a more realistic estimate of the dietary intake of pesticide residues;
- to establish MRLs for residues in processed products where necessary, according to the requirements of national regulatory authorities or international standards.

The effects of food processing on pesticide residue levels may also be influenced by the physical location of the pesticide residue as well as the physical-chemical properties of the pesticide such as solubility, volatility, hydrolytic rate constants, water–octanol partition coefficient (*Kow*) and thermal degradation (Holland et al., 1994; Kaushik et al., 2009). However, more research is required on some of these fundamental physical-chemical processes in the context of food processing. The techniques used for the evaluation of the fate of pesticides during food processing have been critically reviewed by González-Rodríguez et al. (2011c) to determine those areas where improvements are needed or desirable. This study led to know that removal/concentration of residues in food by processing is affected by type of food, pesticide type and nature and severity of processing procedure used.

Production of safe and healthy food is a key priority in the EU and worldwide. In the light of increasing reports on pesticide contamination of food commodities (Rial-Otero et al., 2007; González-Rodríguez et al., 2008; Berrada et al., 2010; Chen et al., 2011; Claeys et al., 2011;

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Hjorth et al., 2011; Latif et al., 2011; LeDoux, 2011; López-Fernández et al., 2012), regulatory authorities, consumers and buyers are becoming more aware of the importance of safe and high quality food products not only during primary production, but also throughout all stages of the food chain. Thus, studies into effects of storage and some commercial processing techniques on residues in food are becoming an important part of the registration requirements for pesticides in many countries. The Joint FAOWHO meeting on pesticide residues (JMPR, 1991) considers effects of processing as part of their reviews of residue data for particular pesticides. Some governments are also considering the introduction of formal protocols to evaluate effects of typical domestic food preparation (Holland et al., 1994). The US food industry has published some data showing large reductions in residue levels during commercial processing of vegetables (Elkins, 1989). The United States Department of Agriculture (USDA) has also established the Pesticide Data Program (PDP) that is a national pesticide residue database program (http://www.ams.usda.gov/AMSv1.0/). PDP manages the collection, analysis, data entry, and reporting of pesticide residues on agricultural commodities (fresh and processed) in the US food supply. The effects of processing on pesticide residues in food have been the subject of several reviews published over the last years (Cabras and Angioni, 2000; Kaushik et al., 2009; Keikotlhaile et al., 2010; Bajwa and Sandhu, 2011; González-Rodríguez et al., 2011c).

In this context of increasing concern on the pesticide residue levels in ‘‘processed foods’’ from ‘‘primary food commodities’’, it is interesting to study the loss of pesticide during the fermentation process in order to re-evaluate MRLs on such commodities (**Table 2**). The objective of the present review was therefore to investigate the dissipation of different pesticides during fermentation as well as to study the effect of pesticides on the yeast growth, which

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indicates the efficiency of fermentation. This kind of study is among the critical supporting studies required for more realistic estimates of the dietary intake of the pesticides. The data of such study may be useful in estimating ‘‘processing factors’’ for the management of pesticide residues, which would contribute to formulate regulatory guidelines for fixing and re-evaluating of maximum residue limits on those fermented products. Recommendations are also given on those research challenges facing the study of the effects of fermentation on pesticide residues, as well as the effects of residues on fermented food quality (mainly aroma) and safety.

2. Influence of food fermentation on pesticide degradation

Biodegradation, biotransformation, and biocatalysis are terms dealing with the same concept: microbial metabolism. This term is used depends on the interest of the persons studying it. If their interest is in degrading environmental pollutants, they are said to study biodegradation. An industrialist using microbial metabolism is said to be conducting a biotransformation or to be using biocatalysis. In some cases, these interests can even overlap (**Figure 1**).

Food can be a vehicle for chemical hazards, whether naturally present in the food (e.g. cyanide) or contaminating the food as a result of poor agricultural practices (e.g. pesticide residues) or environmental pollution (heavy metals, dioxins). Food processing technologies can be applied to increase digestibility, enhance the edibility of food, intensify sensory properties, increase shelf life or improve nutritional quality, but also to render food safe (Motarjemi, 2002). Fermentation is often part of a sequence of food processing operations, such as cleaning, grinding, soaking,

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salting, cooking, packaging, and distribution. Fermentation is a simple process during which the enzymes hydrolyze most of the proteins to amino acids and low molecular weight peptides; starch is partially converted to simple sugars which are fermented primarily to lactic acid, alcohol and carbon dioxide (Pardez-López et al., 1991). The potential of fermentation for improving the nutritional quality and safety of foods should therefore be viewed within the context of the complete food processing operation. Consideration must be given also to the effect (including changes to bioavailability) of fermentation on environmentally acquired (in food and soil) chemical contaminants, such as heavy metals, trace elements, and pesticides.

Reductions of pesticide levels during fermentation could mainly be due to chemical or biological degradation (Aislabie and Lloyd-Jones, 1995; Azizi, 2011), rather than the absorption onto the microbial cell walls (Ruediger et al., 2005). Biodegradation of chemicals by microorganisms is one of the most important mechanisms for the breakdown of many organic compounds (Spanggord et al., 1991; Sato, 1992; Boethling, 1993; Bayarri et al., 1997). Extracellular enzymes of the bacteria are capable of cleavage a broad range of chemical pesticides. For instance, it was observed that a diverse group of bacteria, including members of the genera *Alcaligenes*, *Flavobacterium*, *Pseudomonas* and *Rhodococcus*, are able to metabolize pesticides (Aislabie and Lloyd-Jones, 1995). These microorganisms use the pesticides as their carbon and energy sources. In addition to the natural structure of the pesticides, their volatility and adsorption ability to matrix compounds are also important factors affecting sensitivity to the biological cleavage (Langlois et al., 1970; Azizi, 2011). These factors themselves are dependent on a wide range of environmental parameters such as temperature, light, moisture and pH (Aislabie and Lloyd-Jones, 1995; Azizi, 2011). In many cases, stability of these pesticides to the biological destruction arises from their insolubility in water, as the microorganisms are incapable of decaying such materials. Higher moisture increases degradation rate of the water soluble pesticides by the microorganisms, while reduces their volatility (Azizi, 2011). In addition, the degradative role of these microorganisms accelerates in association with yeast present in the medium (Oshiro et al., 1996). Therefore, isolation, identification and screening of the microorganisms which are capable of pesticides residue degradation in food are important issues.

Numerous researches about the impact of the microorganisms in the degradation of the pesticides have been done regarding qualitative and quantitative aspects of this phenomenon. Yeast and other microorganisms have shown the ability to degrade some pesticides belonging to pyrethroid (Fatichenti et al., 1983 and 1984), organochlorine (Ledford and Chen, 1969; Mirna and Coretti, 1979; Peric et al., 1981; Boethling, 1993; Abou-Arab, 1997; Bayarri et al., 1997; Nawab et al. 2003) and organophosphorus groups (Cabras et al., 1995a,b,c; Karpouzas et al., 2005; Azazi, 2011).

Several studies about the fermentation impact on dissipation of pesticide residues from different commodities of vegetal and animal origin were published in the last years (**Table 3**), although most references are for liquid foods, as compared to solid foods, and mainly for alcoholic beverages such as wine.

Fruits and vegetables. Reduction of the levels of parathion was observed when apple juice fortified at 25 mg/kg was processed into cider and vinegar (Banna and Kawar, 1982). After a fermentation period of 12 days, the levels of parathion in the supernatant cider decreased about 70% while in the vinegar formed after 57 days of fermentation the reduction was about 80%.

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Recently, Azizi (2011) studied the effects of isolated indigenous microflora from Iranian vegetable source on the degradation of containing pesticides residue during the fermentation process. After 48 h of fermentation, the concentration of malathion considerably decreased (14% of the initial concentration in the unprocessed sample) whereas, diazinon concentration only decreased about 17%. The remarkably degradation of the malathion during the fermentation could be attributed to its instability at low pH ranges (Freed et al., 1979), regardless of bacterial decomposition.

Wines. During the manufacture of wine, in addition to the transfer of residues from the grapes into the must, stability of residues to the fermentation and fining processes are important factors. Fermentation on the skins as carried out in red wine production is likely to lead to higher residues in raw wine. Residues in must may be absorbed to the solids produced during fermentation and thus be lost in the fining processes. However, a range of pesticides with suitable solubilities and stabilities can give rise to residues in wine (Holland et al., 1994). The effect of the vinification process on the dissipation of parathion (Kawar et al., 1978), dialifor, methidathion and dimethoate (Kawar et al., 1979) in artificially fortified grape juice prior to alcoholic fermentation was evaluated. The finished wine after 56 days contained 35% of parathion, 10% of dialifor, 46% of methidathion and 85% of dimethoate added to the grape must. About 50–80% of the methiocarb residues on grapes treated with a concentrate sprayer were removed from the vinification process with pomace and additional reductions occurred during the settling of juice. Fatichenti and coworkers observed that deltametrin, permethrin and fenvalerate were completely degraded after fermentation with *Saccharomyces cerevisiae* that can be attributable to the yeast activity, while the fungicides benalaxyl, folpet, furalaxyl, metalaxyl, iprodione, procymidone, and ofurace remained unaffected (Fatichenti et al., 1983 and 1984). Total residues in wines made from grapes treated with methiocarb seven days before harvest was 4.9 mg/kg in white Riesling wine and 4.6 mg/kg in Pinot noir wine which represented 26% and 13% of the initial residues on grapes (Miller et al., 1985). According to Cabras et al. (1995c), grape processing into wine (obtained after 15 days) caused considerable residue reduction for chlorpyrifos methyl (81%), parathion methyl (86.5%) and quinalphos (82%), moderate reduction for methidathion (62.5%) and almost no reduction for fenthion (<25%). In addition, Cabras et al. (1998) observed negligible residues of fluazinam, mepanipyrim and tetraconazole after wine making (15 days). This was due to fermentation in case of fluazinam and mepanipyrim and to removal during the formation of must in the case of tetraconazole. The effect of red wine malolactic fermentation on the fate of seven fungicides (carbendazim, chlorothalonil, fenarimol, metalaxyl, oxadixyl, procymidone, and triadimenol) and three insecticides (carbaryl, chlorpyrifos, and dicofol) was investigated by Ruediger et al. (2005). Malolactic fermentation using *Oenococcus oeni* resulted in significant reduction in chlorpyrifos and dicofol concentrations which were reduced by 70% and 30%, respectively, whereas the concentrations of chlorothalonil and procymidone diminished only slightly.

Meat. The effect of the fermentation process in the dissipation of pesticide residues from meat products was also studied. Mirna and Coretti (1979) found that in the presence of a starter culture and a nitrite curing salt, the levels of DDT (1,1,1-tricloro-2,2-bis(4-clorofenil)-ethane) and γ-HCH (γ- hexachlorocyclohexane or lindane) in dry sausage final product were 76% and 77% of the initial concentrations, after 38 and 30 days respectively. Later, Peric et al. (1981) studied the biological decomposability of organochlorine pesticides in fermented sausages observing that

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DDT (mainly) and HCH (partially) can be degraded by the species of *Debariomyces*, *Micrococcus* and *Lactobacillus*; showing *Lactobacilli* the lowest effect. Authors also perceived that adding the microbial mix to the fermented sausage led to the significant decrease in HCH concentration. Investigations reported by Ariño et al. (1992, 1993, 1995) demonstrated that sausage curing for 1 month caused a 30% reduction in naturally occurring lindane levels, whereas residues of α-HCH in meat decreased by almost 25%. These reductions were attributed to a possible microbial degradation by the fermented meat microflora. On the other hand, the hexachlorocyclobenzene (HCB) and 1,1-dichloro-2,2bis(p-chlorophenyl)ethylene (*p,p'*-DDE) contents were not significantly reduced after curing. Abou-Arab (2002) observed that the residues of DDT and lindane were reduced by 10% and 18%, respectively, in fermented sausage after 72 h of fermentation. The results confirmed that these reductions were due to the activity of meat starter. In addition, in vitro studies indicated that culture media *Micrococcus varians* metabolized DDT mainly to DDD (1-chloro-4-[2,2-dichloro-1-(4-chlorophenyl)ethyl]benzene) and lindane mainly to 2,4-, 2,5-, 2,6- and 3,4-dichlorophenol; 2,3,4- and 2,3,5-trichlorophenol; hexachlorobenzene; and pentachlorophenol within 15 days (Abou-Arab, 2002). On the contrary, the insignificant role of *Lactobacillus plantarum* in degrading p,p′-DDT and lindane was observed (Abou-Arab, 2002).

***Dairy products*.** Almost complete degradation of DDT and DDE in the Roquefort blue cheese by using different species of gram positive *Lactobacilli*, *Streptococci* and yeasts were reported by Ledford and Chen (1969). Abou-Arab (1991) indicated that gram-positive lactic cultures were unable to cause any measurable degradation of aldrin, DDT or γ-BHC. However, the isolated Ras cheese microorganisms reduced the total DDT residues by 10.8, 11.8 and 4.8% for

Streptococci, lactobacilli and yeasts, respectively, at the end of the incubation period (Abou-Arab, 1997). On the contrary, an increment in the levels of DDD and DDE during incubation was observed, that may be due to the degradation of DDT into DDD and DDE. The degradation of seven organophosphate pesticides-OPPs- (dimethoate, fenthion, malathion, methyl parathion, monocrotophos, phorate and trichlorphon) in bovine milk during yoghurt processing was studied by Bo and coworkers (2011). The bovine milk was spiked with the pesticides and fermented with two commercial directed vat set starters at 42 °C. An influence of the starters in the degradation of the pesticides during yoghurt processing was observed when compared to the degradation of these pesticides in the control sample. In addition, the two starters showed different influence on the degradation process. Thus, the degradation of dimethoate, fenthion and trichlorphon in the milk during yoghurt processing increased when either of the two starters was added, leading to a larger rate constant of degradation or a shorter half-live period of these pesticides. The starter from Rhodia also accelerated the degradation of methyl parathion, monocrotophos and phorate but the starter from Danisco had little or no impact on the degradation of these three pesticides. With respect to malation, the degradation in the milk was not enhanced by the starters, because its rate constant of degradation in the milk fermented with two starters was lower than that in the control. Very recently, Zao and Wang (2012) investigated the impact of *Lactobacillus* spp., including *L. bulgaricus*, *L. paracasei* and *L. Plantarum*, on degradation kinetics of the same OPPs (dimethoate, fenthion, malathion, methyl parathion, monocrotophos, phorate and trichlorphon). After a culture time of 24 h at 42 ºC, the decrease levels of the OPPs ranged from 20.9% (methyl parathion, incubated with *L. paracasei*) to 46.9% (malathion, incubated with *L. plantarum*). According to the results, *L. bulgaricus* exhibited stronger enhancing impact on the degradation of dimethoate, fenthion and monocrotophos while *L. plantarum* gave stronger enhancing impact on the degradation of malathion, methyl parathion and trichlorphon.

As stated above, food processing leads to large reduction in pesticide levels in most cases. Although there are some situations in which pesticide degradation might lead to metabolites or by-products with similar or higher toxicity than their parent compounds (Zao and Wang, 2012) and they can persist during fermentation. Degradative or transformation processes leading to formation of metabolites will often be increased by unit operations used in food processing, particularly those involving use of heat or chemicals (Holland et al, 1994). Although no examples are available of pesticides where food processing has resulted in the production of new metabolites, the proportions of various metabolites may change from those found in field or laboratory studies on whole plants. As metabolites are generally more polar than parents, changes in proportions between processing fractions also can be expected. Therefore, research on metabolites is critical to understand the degradation processes of pesticide residues. The ethylene bisdithiocarbamate (EBDC) or propylene bisdithiocarbamate (PBDC) fungicides are often used to illustrate the formation of toxicologically relevant metabolites during processing procedures. The conversion of EBDCs and PBDCs into ethylenethiourea (ETU) and propylenethiourea (PTU) is particularly favored by high pH and heat (Timme and Waltza-Tylla, 2003) although the formation of ETU by thermal degradation in aqueous media can be greatly reduced by the addition of copper sulphate by the formation of a stable cupric EBDC complex (Lessage, 1980). ETU and PTU are EBDC and PBDC degradation products with carcinogenic effects (Nitz et al., 1984).

Only on fermented beverages, relevant metabolites have been identified during processing procedures but not only attributed to fermentation. A study carried out with hops treated with radiolabeled EBDCs showed that parent fungicides (maneb/propineb) are mainly changed to ETU/PTU (Lesage, 1980). ETU residues have been detected in beer as a consequence of the high usage of EBDC fungicides on hops. Banna and Kawar (1982) detected the presence of two metabolites of parathion (aminoparathion and 4-nitrophenol) in cider. The behavior of some s-triazine herbicides and metabolites ([14C]atrazine, [14C]deethylatrazine, [14C]-deisopropylatrazine, [14C]hydroxyatrazine, [14C]terbutylazine, and deethylterbutylazine) during beer production was studied (Hack et al., 1997). During fermentation hydroxyatrazine (OHA) and hydroxyterbutylazine (OHT) were formed. Monitoring of these herbicides, mainly in the brewing water, is essential because like atrazine these polar degradation products are classified as possible human carcinogens (Hack et al., 1997). Therefore, studies to characterize the behavior of pesticide residues during brewing are necessary to perform a more realistic dietary risk assessment.

3. Effects of pesticides on food fermentation

Presence of pesticide in substrate is known to affect the microbial growth or the multiplication of microbial population (Cabras et al., 1997a; Abou-Arab, 2002, Sharma et al., 2005). The presence of pesticides has been associated with stuck and sluggish fermentations (Girond et al., 1989; Laruef, 1991; Otero et al., 1993; Cabras et al., 1999 and 2000; Cabras and Angioni, 2000; Ruidiger et al., 2005). These residues can act directly or indirectly to inhibit yeast growth during fermentation (Specht, 2003). In fact, any interruption or delay in the fermentation process can alter the qualitative and quantitative characteristics of the final product (Oliva et al., 1999; Fleet, 2003; García et al., 2004).

Most of the studies about the pesticide effects on yeasts were performed in the beer and wine sector. Antiseptic activity was observed to vary among pesticides (**Table 3**). Whereas some pesticides are shown to have remarkable antiseptic activity on the yeasts and other microorganisms; for other pesticides no important differences were observed between the kinetics of fermentations of differently treated matrices and controls, indicating no inhibition of the microorganisms. Nowadays new pesticides can be traded only after their inactivity on fermentative microflora has been shown (Cabras and Angioni, 2000).

3.1. Effects of pesticides on yeasts

Remarkable antiseptic activity on the yeasts was reported for several organic pesticides belonging to acylalanine (benalaxyl), anilinopyrimidine (pyrimethanil), benzimidazole (methyltiophanate and benomyl), carbamate (mancozeb and maneb), organochlorine (dicofol, DDT, endosulfan and lindane), phenylsulphamide (dichlofluanid), phenylurea (diuron), phtalimide (captafol, captan and folpet), pyrimidine (fenarimol), and triazole (hexaconazole, propiconazole and triadimefon) groups (Peynaud and Lauforcade, 1953; Bolay et al., 1976; Sapis-Domercq et al., 1977, 1978; Gaia et al., 1978; Schopfer, 1978; Lemperle et al., 1982; Conner, 1983; Cabras et al., 1987; Farris et al., 1989; Girond et al., 1989; Dubernet et al., 1990;

Zironi et al., 1991; Cabras and Angioni, 2000; Abou-Arab, 2002; Sharma et al. 2005; Calhelha et al., 2006; Cus and Raspor, 2008) and also for inorganic ones (copper hydroxide and sulphur) (Batusic et al. 1999). For instance, Gaia et al. (1978) reported that phthalimides fungicides, particularly folpet, even at concentrations of 0.1 mg/kg, inhibit yeast cell development and reproduction. Authors also observed that these fungicides affect both quantity and quality of the spontaneous yeast microflora in the grape and must, which reduces the fermentation by *S. cerevisiae*, while increasing the fermentation by *Candida*. Girond et al. (1989) showed that mancozeb, folpet, and myclobutanil were toxic to 284 different yeasts isolated from musts and grapes obtained from four French vineyards during the 1986 and 1987 vintage. Studies conducted with Flor-yeast (*S. cerevisiae* var. *prostoserdivii*) showed that film growth was not complete with benalaxyl tested at concentrations higher than 6 mg/L, and was completely inhibited by triadimefon tested at concentrations higher than 30 mg/L (Farris et al., 1989). Batusic et al. (1999) described the effect of copper hydroxide and sulphur on different types of the species *S. cereivisiae* and *Saccharomyces bayanus*. The addition of these two products rapidly decreased the fermentation activity of *S. bayanus*, while showing a lower intensity of fermentation with *S. cerevisiae*. The study by Sharma et al. (2005) demonstrated that the presence of endosulfan, hexaconazole and propiaconazole in the matrix suppressed the yeast growth in the range 7–33%, 12–44% and 11–40%, respectively (**Figure 2**). The negative effect of benomyl on yeast growth was observed by Calhelha et al. (2006) being *Zygosaccharomyces rouxii* and *S. cerevisiae* the most resistant yeasts, while *Rhodotorula glutinis* was the most susceptible. Cus and Raspor (2008) studied the spontaneous wine fermentation with *S. cerevisiae* and *H. uvarum* with pyrimethanil in the must. This fungicide had an effect on the course and successful conclusion of spontaneous wine fermentation. The initial *S. cerevisiae* concentration was significantly lower, while the *H. uvarum* concentration was higher in the must treated with pyrimethanil.

On the contrary, fermentations had a regular course even though the presence of different concentrations of pesticides belonging to anilide (fenhexamid), anilinopyrimidine (cyprodinil, mepanipyrim and pyrimethanil), azole (tebuconazole and tetraconazole), benzimidazole (benomyl), carbamate (carbendazim and methiocarb, metiram), dicarboximide (chlozolinate, iprodione, procymidone, and vinclozonil), organophosphate (chlorpyrifos, chlorpyrifos-methyl, malathion, methidathion, methylparathion, fenitrothion), phenylamide (metalaxyl), phenylsulphamide (dichlofluanid), pyrethroid (deltamethrin), pyridine (fluazinam), pyrrole (fludioxonil), quinoline (quinoxyfen), strobilurine (azoxystrobin) groups (Cordier, 1954; Lemperle et al., 1970 and 1971; Bolay et al., 1972; Gnaegi and Dufour, 1972; Minarik and Regala, 1975; Schopfer, 1978; Sapis-Domercq, 1980; Conner, 1983; Farris et al., 1989; Cabras et al., 1995a, 1995c, 1997b, 1998, 1999, 2000, 2001, 2003a; Sala et al., 1996, Fort et al., 1999; Ochiai et al., 2002; López et al., 2004; Sharma et al., 2005; González-Rodríguez et al., 2009b). For instance, carbendazim residues at concentrations higher than 1.5 mg/L did not affect the film growth of Flor-yeast belong to the *S. cerevisiae* var. *prostoserdivii* (Farris et al., 1989). Sapis-Domercq (1980) verified that the presence of metalaxyl iprodione, procymidone, and vinclozonil did not affected on activity of several yeasts (*S. cerevisiae*, *S. bayanus*, and *balii*; *Hanseniaspora uvarum*; *Candyda mycoderma*). Quinoxyfen showed no effect on the alcoholic fermentation using three strains of *S. cerevisiae* (1043, 1090, and 1189) (Cabras et al., 2000; Lopez et al., 2004). The presence of some fungicides (azoxystrobin, cyprodinil, fludioxonil, mepanipyrim,

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pyrimethanil, and tetraconazole) having low fungal toxicity, even at high concentration levels does not affect the alcoholic fermentation by *S. cerevisiae* and *Hanseniaspora / K. apiculata* (Cabras et al., 1995a, 1995c, 1997b, 1998, 1999). This was due to the presence of a sufficient number of cells in all of the samples to allow a regular fermentative process (Sharma et al., 2005). On the contrary, presence of some of them stimulated the yeasts, and especially, *Hanseniaspora / K. Apiculata*, to produce more alcohol (Cabras et al., 1999). Since fenhexamid can be easily degraded by UV or sunlight irradiation, yielding 7-chloro-6-hydroxy-2-(1-methylcyclohexyl)-1,3-benzoxazole (CHB) as a main photoproduct, CHB was isolated, and its effect on alcoholic fermentation of *Saccharomyces cerevisiae* was also studied. Similar to what was found for fenhexamid, the CHB photoproduct does not affect alcoholic fermentation (Cabras et al., 2004). Tests were also performed to check whether the presence of tetrahydrophthalimide (THPI), a captan metabolite, could have a negative effect on the fermentative microflora (Cabras et al., 2003b). Fermentation tests were carried out with the addition of a known quantity of THPI (4 mg/kg) on untreated grapes and the must was left to ferment without any yeast addition. Fermentation had a regular course, and no significant differences were observed between the samples with THPI and the control samples. Results obtained by González-Rodríguez and coworkers (2009b) seems to indicate that *Saccharomyces cerevisiae* is not negatively affected by tebuconazole, as also reported by other authors with this microorganism and other fungicides like iprodione and fludioxonil (Ochiai et al., 2002).

3.2. Effects of pesticides on bacteria

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Scarce studies have directly or indirectly investigated the effect of pesticide residues on the rate of malolactic fermentation (Haag et al., 1988; Bordons et al., 1998; Cabras et al., 1987, 1994b, 1999; Cabras and Angioni, 2000). Although studies on lactic acidic bacteria inhibition by pesticides (Haag et al., 1988; Cabras et al., 1994b; Bordons et al., 1998, Vidal et al., 2001) report minimum inhibitory concentrations for various pesticides ranging from as low as 1 to > 30 mg/L, in most cases pesticide residues were found to have little or no effect on malolactic fermentation (Sapis-Domercq, 1980; Haag et al., 1988; Cabras et al., 1994a, 1994b, 1999; Sala et al., 1996; Ruediger et al., 2004, 2005; Sharma et al., 2005; González-Rodríguez et al., 2009b). Some of the most relevant studies are now described. High levels of some pesticides such as malathion, parathion-methyl, fenitrothion, dichlofluanid, chlorpyrifos, vinclozolin, chlozolinate, procymidone, iprodione, deltamethrin and copper oxychloride did not affected the malolactic fermentation (Sala et al., 1996, Sharma et al., 2005). Vidal and coworkers (2001) studied the inhibitory effect of copper and dichlofluanid, on *Oenococcus oeni* and malolactic fermentation in simulated wine. The minimal inhibitory concentrations that affected malolactic fermentation were just under 5 mg/L, which was enhanced by ethanol. Inhibition was due mainly to a decrease in cell number but not to lower specific malolactic activity. Ruediger and coworkers (2004, 2005) evaluated the effect of red wine malolactic fermentation on the fate of seven fungicides (carbendazim, chlorothalonil, fenarimol, metalaxyl, oxadixyl, procymidone and triadimenol) and three insecticides (carbaryl, chlorpyrifos, and dicofol). Malolactic fermentation was generally unaffected by the presence of pesticide residues except in the case of dicofol, where only 6−13% of the malic acid was metabolized. Dicofol can be hydrolyzed to the corresponding benzophenone and chloroform, and the parent compound, the hydrolytic products, or a

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combination of all three compounds could have a detrimental effect on the bacteria. Chlorothalonil and fenarimol showed only a minor effect on the conversion of malic acid to lactic acid (82−84% metabolized), whereas chlorpyrifos at the lower concentration showed a similar effect (76% malic acid metabolized). Malolactic fermentation for the controls without carbendazim was 95% complete, whereas malolactic fermentation for the controls for the other pesticides was 80% complete on the basis of the criterion that 0.1 g/L of malic acid is considered as complete. Recently, González-Rodríguez and coworkers (2009b) also observed the resistance of the bacteria *Oenococcus oeni*, used in the malolactic fermentation, to the tebuconazole concentration remaining in the wine after the first stage of alcoholic fermentation (0.6 mg/L).

4. Pesticides and sensory quality of fermented foods

The sensory quality of fermented products is essential to gain the consumer's attention. Therefore, it is crucial to study the factors affecting the appearance, color, taste, and texture of the product, as well as its relationship to the sensory attributes perceived by consumers.

As stated above, the presence of some pesticide residues may negative affect the growth and development of certain microorganism (yeasts and bacteria) and therefore delay or stuck (incomplete, arrested) the fermentation. This is one of the main problems that can arise during fermentation. By definition, a stuck fermentation is a fermentation that has stopped before all the available sugar in the must has been converted to alcohol and CO_2. The serious dangers arising from the premature arrest of fermentation are well known. Generally, residual sugar in beer and wine is a dangerous and undesirable condition. If sugar is still present, bacteria may multiply and increase volatile acidity. Sometimes, fermentation resumes after the fermented beverage is bottled, and the yeast produces unsightly sediment in the bottle. The main causes of stuck and sluggish fermentation are restriction of nutrients, decrease in oxygen availability, exposure to high temperatures, low pH values, accumulation of ethanol during the must fermentation by yeasts and the brewing practices followed, but also the presence of toxic substances like pesticide residues (Bisson, 1999). Stuck and sluggish fermentation could also alter the concentration of some compounds responsible for the sensory quality of fermented food in general and the aroma in particular, such as it is explained below. Although, there are studies on fermented dairy products, olives and beers, most of the scientific studies dealing with the effect of pesticides on the sensory quality of fermented foods were relative to wines, and mainly to their aromatic defects (**Table 3**).

4.1. Pesticides effects on physical-chemical parameters

Zidan et al. (1990) investigated the susceptibility of some lactic acid bacteria to different insecticides in skim milk. Authors reported the reduction (%) of lactic acid produced by *L. bulgaricus* (12-44%), *L. helveticus* (18-20%), *St. lactis* and *St. thermophiles* (12-31 %) at the end of incubation period in the presence of fenvalerate, malathion and DDT. Exceptionally, fenvalerate increased acid production by *L. bulgaricus* (17%) particularly after 72 h incubation and up till the end of the incubation period (120 h). Recently, Abou Ayana *et al.* (2011) investigated the effect of two fungicides (mancozeb and metalaxyl), herbicides (glyphosate isopropylammonium and thiobencarb) and insecticides (chlorpyrifos-methyl and methomyl) on the acid production by certain lactic acid bacteria (*Streptococcus salivarius* subsp. *thermophilus* H, *Lactobacillus acidophilus*, *Lactobacillus casei* subsp. *casei*, *Lactobacillus delbrueckii* subsp. *bulgaricus* and *Bifidobacterium* spp. 420). Authors observed that all tested pesticides had a slight effect in acid production at concentrations lower than 4 mg/kg. Insecticides caused the greatest harmful effect on acid production by all organisms studied followed by herbicides and fungicides.

Studies by Navarro and coworkers (2007a and 2007b) studied the variability in the fermentation rate and color of young lager beer as influenced by insecticide (pendimethalin and trifluralin), herbicide (fenitrothion, malathion, and methidathion) and fungicide (fenarimol, myclobutanil, nuarimol and propiconazole) residues. The alcohol content (% by volume) of young lager beer at the end of fermentation was sensibly lower in the sample containing propiconazole (1.4%), fenitrothion (4.5%) and trifluralin (4.4%) residues than in those spiked with myclobutanil (5.0%), malathion (5.2%), nuarimol (5.2%), methidathion (5.4%), pendimethalin (5.4%) and fenarimol (5.4%), while in the control sample, the alcohol content was 5.5%. These results show that propiconazole, fenitrothion and trifluralin affect the growth and fermentability of brewer's yeast, influencing the fermentative kinetics and causing stuck fermentation from the high krausen phase. A higher amount of residual sugars (glucose, fructose, maltose and maltotriose) was found after fermentation in the samples treated with fenitrothion and trifluralin. In addition, propiconazole had a marked influence on the assimilation of glucose, maltose and maltotriose by

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the yeasts. Significant differences in beer color and in the mean pH values (especially for propiconazole 3.0 *vs.* 4.1 for the control sample) at the end of the fermentation were also observed in all cases for the treated samples in comparison with the control sample. This finding is important because pH values below 4.0 cause an acidic beer taste, and acidification by microbial infections during fermentation must be avoided. Therefore, the presence of propiconazole alters sensibly the final quality of the beer. More recently, the same authors studied the effect of sterol biosynthesis-inhibiting fungicides (cyproconazole, diniconazole, epoxiconazole, flutriafol, and tebuconazole) on the quality of young ale beer (Navarro et al., 2011). The alcohol content at the end of fermentation was substantially lower in the sample containing diniconazole (4.1%), epoxiconazole (4.1%), cyproconazole (4.3%), tebuconazole (4.3%) and flutriafol (4.5%), while in the control sample the alcohol content was 4.6%. In addition, a higher amount of residual sugars (mainly maltose and maltotriose), lower color intensity and higher tint was found in treated beers. However, in this case, at the end of fermentation no influence on the pH values was observed with either of the studied fungicides.

Randazzo and coworkers (2011) observed that the use of kaolin and copper based products (crop protectants used in organic agriculture) can alter the physical-chemical parameters of table olives during fermentation. Thus, final pH and titrable acidity values were slightly higher in treated samples in comparation to the control sample (**Figure 3**).

4.2. Pesticides effects on the polyphenolic content

Until now, studies to evaluate the influence of pesticides on the polyphenolic content of food are scarce in the literature. Only some works focused on wine (Dugo et al., 2004), beer (Navarro et al., 2007a, 2007b, 2011) and table olives (Randazzo et al., 2011) have been published.

Dugo et al. (2004) determined the phenolic (resveratrol, piceid and flavonoids) content in wines from three different Italian regions, obtained from grapes treated with several pesticides and studied the probable influence of the different treatments on the quality of the wines. The results showed that the antioxidant activity of the wine samples was correlated to the amount of phenolic compounds but the individual phenolic compounds in these three regions was not homogeneous and the values were not correlated to the different pesticide treatments.

The content of polyphenols in the beer is very important because they are important antioxidants, mainly lower molecular weight polyphenols. Generally, in beer, 70–80% of the polyphenol fraction originates from barley malt and another 20–30% from hop. In beer, polyphenols contribute up to 60% of the endogenous reducing power (Navarro et al., 2011). Navarro et al. (2007a and 2007b) observed, in young lager beers, significant differences in the total polyphenol content after fermentation for samples containing residues of propiconazole (reductions of 70.8%), myclobutanil (43.0%), fenitrothion (13.6%) and trifluralin (6.8%) with respect to the control, while no influence of fenarinol, malathion, methidathion, nuarimol and pendimethalin were observed. In addition, no significant differences on the total polyphenolic content of young ale beers were observed after fermentation between treated samples with biosynthesis-inhibiting fungicides (cyproconazole, diniconazole, epoxiconazole, flutriafol, and tebuconazole) and control samples (Navarro et al., 2011). An important detriment in the flavonoid content after fermentation was also found for propiconazole with reductions of about 52.3% (Navarro et al., 2007b).

Randazzo and coworkers (2011) observed that in untreated table olives, oleuropein (the major phenolic component of the pulp of green olives) was rapidly hydrolyzed into hydroxytyrosol and elenolic acid by β-glucosidase activity of lactic acid bacteria (LAB) starters. Different trend was registered in the kaolin and copper treated samples, where the concentration of this glucoside compound in brine increased throughout the fermentation, maintaining values between 10 and 20 mg/L. This could be due to the pesticide treatments, which reduced the permeability of the olive skin, inhibiting the diffusion of phenolic compounds into the brine. This could justify the low hydroxytyrosol concentrations (around 40 mg/L) registered in almost all samples with the exception of the untreated samples inoculated with the starters (120 mg/L in the sample inoculated with *L. casei* and 90 mg/L in the sample inoculated with *L. plantarum*).

4.3. Pesticides effects on the aromatic profile

To the best of our knowledge, studies versed on pesticide effects on the aromatic profile of food are principally focused to wine (Aubert et al., 1997, 1998; Oliva et al., 1999, 2008; Darriet et al., 2001; García et al., 2004; González-Rodríguez et al., 2011b; Noguerol-Pato et al., 2011; González-Álvarez et al., 2012); although some works on dairy products (Abou Ayana et al., 2011), virgin olive oils (Benincasa et al. (2008) and table olives (Randazzo et al., 2011) were developed recently.

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As known, wine aroma is due to a series of volatile compounds recognized by the senses of taste and smell. Some of these arise from the grapes and are responsible for what is known as varietal aroma. However, most of them arise from the fermentation process and their concentrations are essentially dependent on the yeasts that predominate during fermentation and the conditions under which fermentation takes place (Steger and Lambrechts, 2000). **Table 4** shows the main volatile compounds and their origins, their typical concentrations in wines, and the characteristics of the aroma produced. All of these elements are described in greater detail in the review by Lambrechts and Pretorius (2000). The current knowledge on the effect of pesticide residues on these aromatic compounds in wine is discussed in the following subsections.

Terpenes. Terpenes, which are present in grape skin and related to sugars, play a significant role in the odor of varietal wines and contribute substantially to grape bouquet. They can be used for accurate varietal characterization (Mateo and Jiménez, 2000).

Phytosanitary treatments with famoxadone, fenhexamid, fluquinconazole, kresoxim-methyl, quinoxyfen and trifloxystrobin under good agricultural practices (GAP) and critical agricultural practices (CAP) showed an increment on the terpenoic group in Monastrell red wine with respect to the control (Oliva et al., 2008). González-Álvarez and coworkers (2012) observed that cyazofamid and famoxadone treatments affected the synthesis of *trans,trans*-farnesol in Godello white wines. Geraniol synthesis was also altered by the use of the new fungicides benalaxyl, iprovalicarb and pyraclostrobin to control downy mildew under GAP in the same experimental vineyard one year before (González-Rodríguez et al., 2011b). This fact could be explained by possible alterations in their biosynthesis, as reported by Oliva et al. (1999) for the major alcohols

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of red wines (Monastrell var.). On the contrary, for other pesticides such as tebuconazole in Mencía red wines no important changes in the terpenoic levels were observed (Noguerol-Pato et al., 2011).

C6 – alcohols. C6-alcohols (1-hexanol, trans-3-hexen-1-ol and cis-3-hexen-1-ol) belong to the group of C6-compounds formed during pre-fermentation steps (harvesting, transport, crushing and pressing of grapes). All have linoleic (C18:2) and linolenic (C18:3) acids as lipid precursors. As a result, they are mainly related to lipoxygenase activity in grapes and/or must aeration, which produces C6-compounds such as C6-aldehydes; these, in turn, can be reduced to C6-alcohols by yeasts during the fermentation process (Cordonnier, 1989).

The synthesis of C6-alcohols, in Godello white wines, was not affected by residual levels of cyazofamid, famoxadone, mandipropamid and valifenalate (González-Álvarez et al., 2012) or residues of the fungicides Cabrio Top, Mikal Premium and Fobeci (González-Rodríguez et al., 2011b). In general, no significant differences with respect to the control wine were registered for 1-hexanol and cis-3-hexen-1-ol (except for grapes treated initially with Fobeci). Similar results were obtained by other authors with chlorpyrifos, fenarimol, mancozeb, metalaxyl, penconazole, vinclozolin, fluquinconazole, kresoxim-methyl, quinoxyfen and trifloxystrobin in Monastrell red wines (Oliva et al., 1999; Oliva et al., 2008); and with fludioxonil and pyrimethanil in Airén white wines (García et al., 2004).

However, the opposite effect was observed for other pesticides. A significant decrease of C6-alcohols was reported with famoxadone and fenhexamid used under critical agricultural practices (CAP) in Monastrell red wines (Oliva et al., 2008); and also with triazole pesticides such as tebuconazole in Mencía red wines (Noguerol-Pato et al., 2011) and fluxilazole in Muscat of Alexandria wines (Aubert et al., 1997). On the contrary, the presence of cyprodinil increased the cis-3-hexen-1-ol level to above their perception threshold (0.07 mg/L) in Airén white wines (García et al., 2004).

Other alcohols. Higher alcohols, which are formed from their amino acid precursors in yeast cells and then transferred to the wine, are responsible for its secondary (fermentative) aroma of wine. There are two broad categories of higher alcohols as regards vinification, namely: aliphatic (propanol, butanol, isoamyl alcohol, isobutanol) and aromatic (2-phenylethyl alcohol and benzyl alcohol). Higher alcohols are typically present at concentrations from 400 to 500 mg/L in wine. Below 300 mg/L, they certainly contribute to the desirable complexity of wine, but above 500 mg/L (Etiévant, 1991), these alcohols —2-phenylethanol excepted— impair wine quality (Rapp and Mandery, 1986).

Studies by Aubert and coworkers (1997) on the effects of fluxilazole on the aroma fraction of Muscat of Alexandria wines reported a decrease in the levels of isoamyl alcohols and 2-phenylethanol, which increases with the treatment dose. A significant decrease of 2-methyl-1-propanol and 3-methyl-1-propanol in Godello white wines was also found when the commercial formulation Mikal Premium (fosetyl-A, mancozeb and iprovalicarb) was applied under GAP, whereas the use of Cabrio Top and Fobeci formulations promote a detriment of the 2-phenylethanol levels (González-Rodríguez et al., 2011b). The lower concentration of these alcohols in the wine can be ascribed to reduced assimilation of the precursor amino acid by yeast

(MacDonall et al., 1984) and/or to alterations in the biosynthesis of the amino acids (Oliva et al., 1999).

In contrast, fungicide treatments with quinoxyfen, trifloxystrobin, cyprodinil, fludioxonil and pyrimethanil, under GAP, produced a significant increase of isoamyl alcohols with respect to the blank causing a decrease in the quality of the final wine (García et al., 2004; Oliva et al., 2008). For other fungicides such as cyprodinil, famoxadone, fludioxonil, fluquinconazole, kresoxim-methyl, mandipropamid, quinoxyfen, pyrimethanil, and trifloxystrobin an increment in the 2-phenylethanol levels was observed (García et al., 2004; Oliva et al., 2008; González-Álvarez et al., 2012). In other studies, no significant differences in the alcohols content was observed between the control wines and those to which the pesticides chlorpyrifos, cyazofamid, famoxadone, fenarimol, mancozeb, mandipropamid, metalaxyl, penconazole, valifenalate and vinclozolin were added (Oliva et al., 1999; González-Álvarez et al., 2012).

Aldehydes. Young wines are poor in aldehydes, the content in which increases slowly during the wine aging process by effect of the oxidation of alcohols. Benzaldehyde and phenylethanal are the two main identified compounds in this group (Perestrelo et al., 2006). In general, published data show that phytosanitary treatments do not affect the aldehyde levels (Oliva et al., 1999, González-Rodríguez et al., 2011b; Noguerol-Pato et al., 2011) or also reduced their synthesis when applied under CAP (González-Álvarez et al., 2012). Nevertheless, Oliva et al. (2008) observed that only when fenhexamid was used under CAP, in Monastrell red wines, the benzaldehyde content increased.

Pesticides (chlorpyrifos-methyl, glyphosate isopropylammonium, mancozeb, metalaxyl, methomyl and thiobencarb) also affected the acetaldehyde and diacetyl production, considered as important constituents of the flavor of fermented milks (Abou Ayana et al. (2011). The highest values of acetaldehyde and diacetyl by yogurt and ABT cultures on the sixth day from cold storing at 6-8 ºC were obtained in control samples (yogurt free pesticides) and decreased with increasing the pesticide concentration. Low pesticide concentrations (2-4 mg/kg) slightly delayed the production of these flavor compounds. However pesticide concentrations of 8 and 10 mg/kg decreased sharply of acetaldehyde and diacetyl production (reductions of about 61-72 % and 76-85 % for yogurt and ABT cultures, respectively).

Esters. The major esters of wine are enzymatically synthesized from alcohols and acids by yeasts during alcoholic fermentation. In the presence of the enzyme alcohol acetyltransferase, acetyl-CoA condenses with higher alcohols to form acetate esters (Peddie, 1990). On the other hand, acyl-CoA formed by fatty acid synthesis or degradation gives fatty ethyl esters by enzymatic ethanolysis (Lambrechts and Pretorius, 2000).

Different studies, applying phytosanitary treatments on grapes, suggested that the ester levels could be affected by the concentration and the nature of these residues (Aubert et al., 1997, 1998; García et al., 2004; Oliva et al., 1999, 2008).

García et al. (2004) registered a decrease in the total levels of ethyl hexanoate, ethyl octanoate and ethyl decanoate when they studied the effect of fungicide residues (cyprodinil, fludioxonil and pyrimethanil) on the aromatic composition of Airén white wines inoculated with different *Saccharomyces cerevisiae* strains. On the contrary, synthesis of these compounds seemed to be activated when the grapes are treated with quinoxyfen, kresomin-methyl and trifloxystrobin (Oliva et al., 2008) or with the commercial formulations Cabrio Top, Mikal Premium and Fobeci (González-Rodríguez et al., 2011b) under GAP. In addition, these commercial formulations also promoted the synthesis of acetate group whereas decreased the levels of ethyl dodecanoate and diethyl succinate in Godello wines (González-Rodríguez et al., 2011b). An increment in the acetate content was also observed by Oliva et al. (2008) for wines with quinoxyfen, kresomin-methyl, famoxadone and trifloxystrobin, whereas fluquinconazole and fenhexamid decreased it.

Isoamyl acetate levels increased in the presence of cyprodinil, fludioxonil, chlorpyrifos, feranimol and vinclozolin (Oliva et al., 1999; García et al., 2004). However, no significant differences were observed in the presence of tebuconazole in Mencia red wines (Noguerol-Pato et al., 2011). With respect to the ethyl acetate content, the presence of chlorpyrifos increased its levels (Oliva et al., 1999) while significantly decreased with famoxadone and fenhexamid (Oliva et al., 2008).

Recently, González-Álvarez et al (2012) did not observe significant differences in ethyl ester and acetate concentrations between the control wine and those from treated grapes with cyazofamid, famoxadone, mandipropamid and valifenalate.

Sulphur compounds. Methionol is one of the less volatile compounds in the sulphur volatile family (Silva Ferreira et al., 2003). When this compound occurs at concentrations above its threshold value (1-2 mg/L), a “cauliflower” aroma is perceived. It is well known that methionine is metabolized with formation of its fusel alcohol (3-methylthio-1-propanol or methionol), its acetate (3-methylthiopropyl acetate), its ethyl ester (ethyl (3-methylthio) propionate) and 3-

ethylthio-1-propanol (Rapp and Mandery, 1986). On the other hand, as it was previously remarked, some authors pointed out that sulphur compounds can also be formed by degradation of sulphur-containing pesticides (Rauhut et al., 1993).

Methionol concentrations decreased significantly in Godello wines treated with the fungicides pyraclostrobin and iprovalicarb (González-Rodríguez et al., 2011b) and in Mencía wines treated with tebuconazole (**Figure 4**) using *Saccharomyces cerevisiae* commercial yeasts (Noguerol-Pato et al., 2011). A similar behavior was observed by Gonzalez-Álvarez et al. (2012) when the fungicides cyazofamid, famoxadone, mandipropamid and valifenalate were applied under CAP.

In addition, the reactivity of copper residues with thiols, mainly during the alcoholic fermentation, had a dramatic effect on the concentration of 4-mercapto-4-methylpentan-2-one and 3-mercaptohexanol in wines (Darriet et al., 2001).

5. Conclusions

Increasing report on pesticide residues in food has caused serious concern among the consumers. Specific scientific investigations are required for understanding the real dietary intake of pesticides and setting up regulatory standards for the management of hazards due to such toxic residues in food commodities. Against this backdrop, processing studies are critical in understanding the real dietary consumption of pesticides. Complementary research should be done about the degrading effects of fermentation on chemical pesticides and possible identification of metabolites. Moreover, it might be interesting to determine the contribution of each fermentative microbiota in the degradation of the pesticides, during the fermentation period. A push in metabolomics to understand the interplay effects of pesticides on fermenting yeasts and bacterias would be of paramount importance, together with advances in extraction protocols and analytical techniques with the use of increasingly sensitive detection equipment technologies to determinate pesticide metabolites.

Sensory quality (appearance, color, odour, taste, and texture) is essential to gain the consumer's attention. In fermented products, stuck or delayed fermentations caused by the presence of pesticides residues have an important impact on sensory quality. In recent years, several studies over the impact of pesticides on sensory quality of wines and beers have been published but it is necessary to extend these studies to other fermented foods. In consequence, there is a need to the development of diagnostic tools to assist food technologists in fermentation practices and the sensory quality of fermented foods, based not only on instrumental analysis of the fermented product but also on sensory analysis by a trained panel to guarantee the consumer´s requirements.

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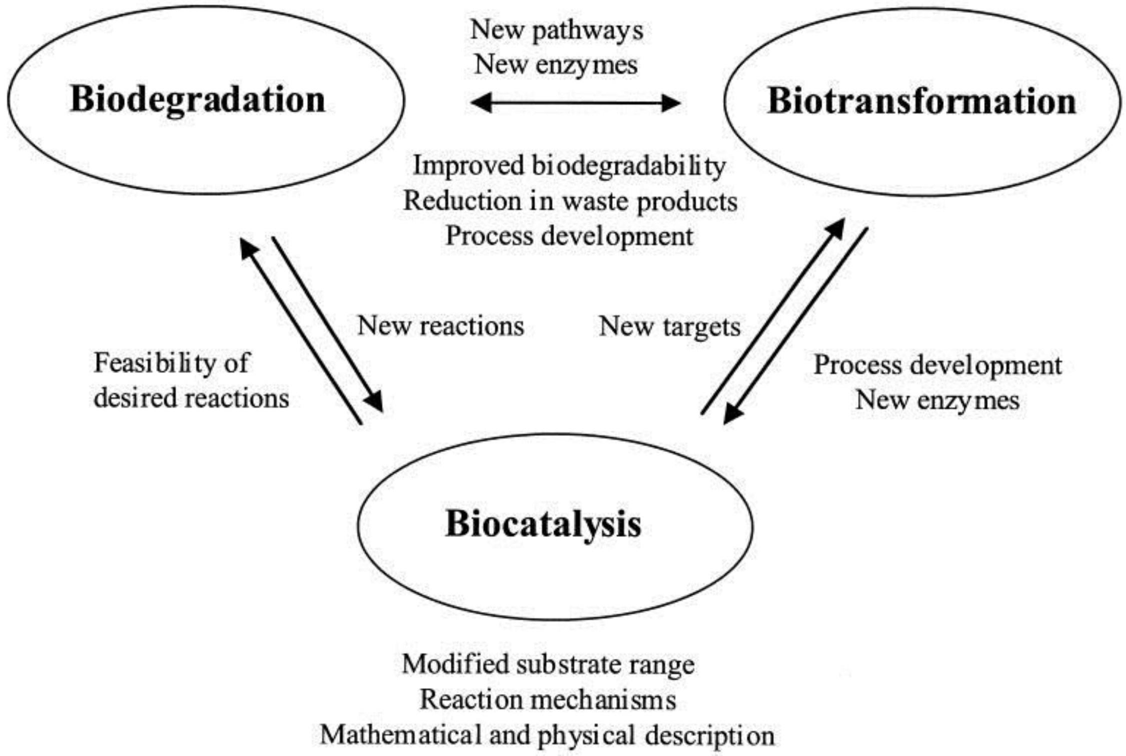
Figure captions:

Figure 1. Interdependence of the three main application areas of enzyme catalysis (reproduced from Parales et al., 2002).

Figure 2. Effect of pesticides on yeast growth (reproduced from Sharma et al., 2005).

Figure 3. Evolution of titratable acidity, expressed as % of lactic acid of treated and untreated table olives (reproduced from Randazzo et al., 2011). Sample identification: untreated and un-inoculated olives (control, sample U-UI); untreated, *L. casei* T19 inoculated olives (sample U-CI); untreated, *L. plantarum* UT2.1 inoculated olives (sample U-PI); kaolin treated, un-inoculated olives (sample K-UI); 5) kaolin treated, *L. casei* T19 strain inoculated olives (sample K-CI); kaolin treated, *L. plantarum* UT2.1 strain inoculated olives (sample K-PI); 7) copper treated, un-inoculated olives (sample C-UI); copper treated, *L. casei* T19 strain inoculated olives (C-CI); and copper treated, *L. plantarum* UT2.1 strain inoculated olives (sample C-PI).

Figure 4. Diagram showing the aroma descriptor profiles of Mencía red wine treated with tebuconazole (wine B) against the control wine (wine A) (reproduced from Noguerol-Pato et al., 2011).



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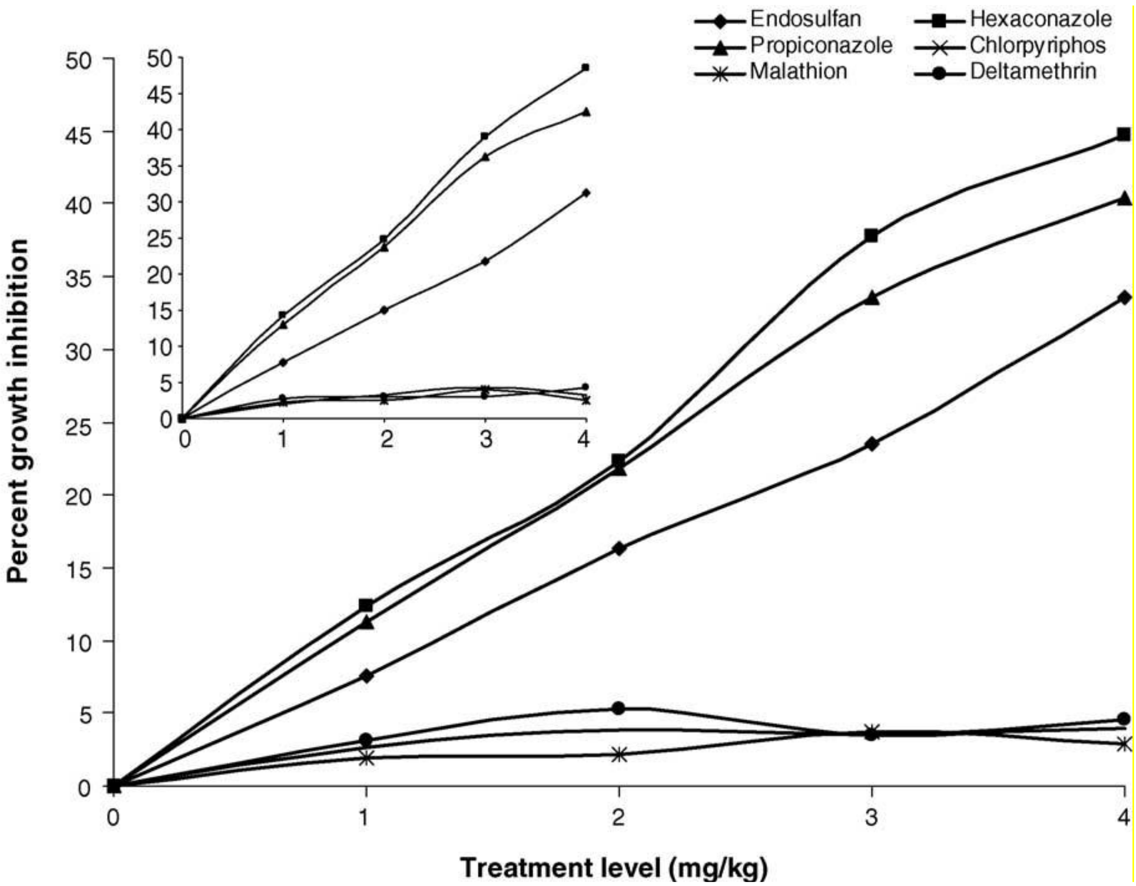

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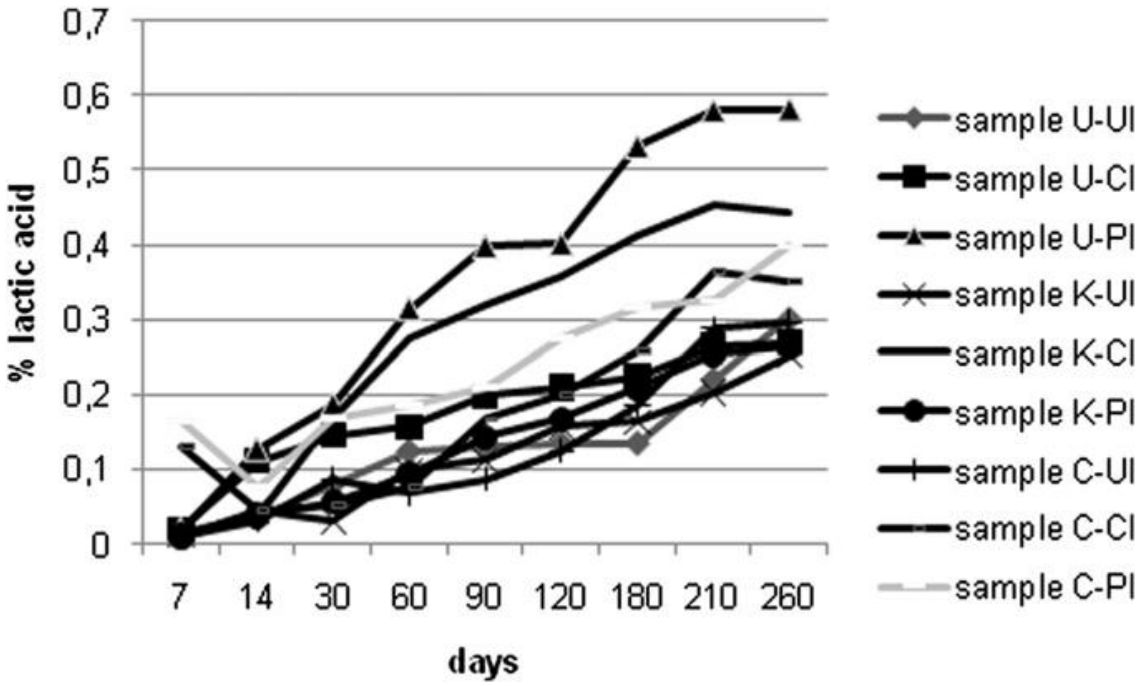

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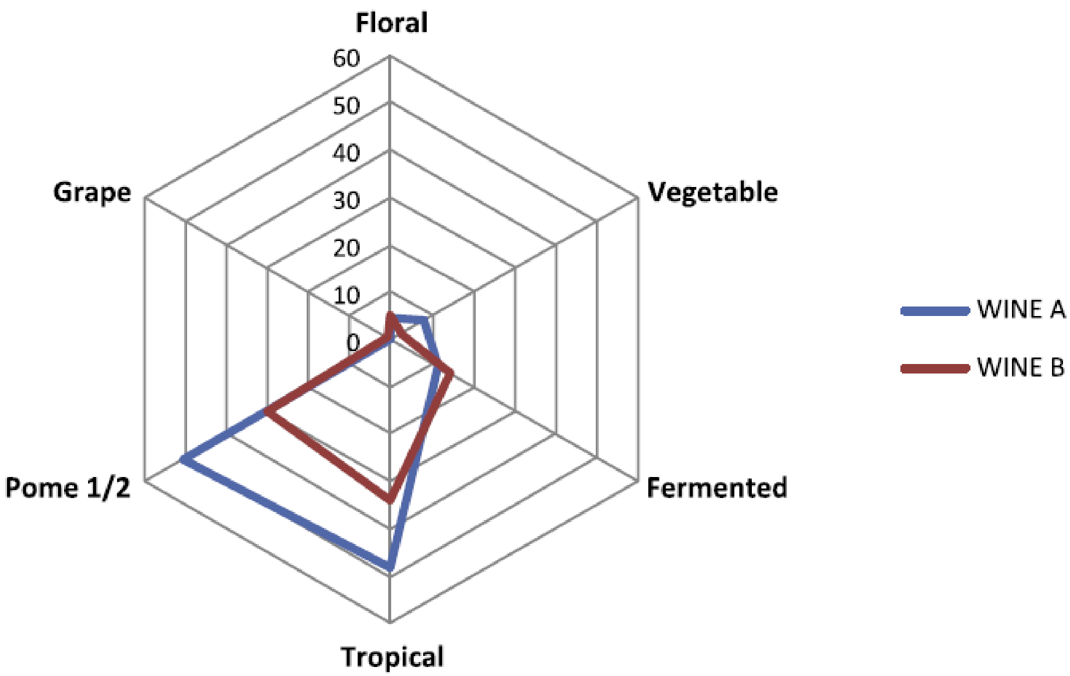

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Table 1: Adverse health effects caused by selected classes of pesticides[a] (Keifer et al., 1996; Meulenbelt and de Vries, 1997; Reeves and Schafer, 2003; Thundiyil et al, 2008).

Chemical/ chemical class	**Examples of pesticides**	**Clinical presentation**	**Route of exposure[b]**
Arsenicals	Arsenic trioxide, CCA, sodium arsenate	Abdominal pain, nausea, vomiting, garlic odour, metallic taste, bloody diarrhea, headache, dizziness, drowsiness, weakness, lethargy, delirium, shock, kidney insufficiency, neuropathy	O, R, D (rarely)
Borates (insecticide)	Boric acid, borax	Upper airway irritation, abdominal pain, nausea, vomiting, diarrhea, headache, lethargy, tremor, kidney insufficiency	O, R, D (broken skin)
Calciferol (rodenticide)	Cholecalciferol, ergocalciferol	Fatigue, anorexia, weakness, headache, nausea, polyuria, polydipsia, renal injury, hypercalcemia	O
Carbamates (insecticide)	Carbaryl, thiram, aldicarb, mecarbam	Malaise, weakness, dizziness, sweating, headache, salivation, nausea, vomiting, diarrhea, abdominal pain, confusion, dyspnea, dermatitis, pulmonary oedema	O, D
Chloralose	Chloralose	Vomiting, vertigo, tremor, myoclonus, fasciculations, confusion, convulsions	O
Chlorphenoxy compounds (herbicides)	Di/tri-chlorophenoxyacetic acid, MCPP	Upper airway and mucous membrane irritation, abdominal pain vomiting, diarrhea, tachycardia, weakness, muscle spasm, coma, acidosis, hypotension, ataxia, hypertonia, seizures, dermal irritation, headache, confusion, acidosis, tachycardia	O, D
Copper compounds (fungicide)	Copper acetate, copper oleate	Abdominal pain, vomiting, skin/airway/mucous membrane irritation, renal dysfunction, coma	O, R, D
Coumarins (rodenticide)	Brodifacoum, warfarin, pindone	Echymoses, epistaxis, excessive bleeding, haematuria, prolonged prothrombin time, intracranial bleed, anaemia, fatigue, dyspnea	O, D (possible)
Diethyltoluamide (insect repellent)	DEET (N,N-diethyl-meta-toluamide)	Dermatitis, ocular irritation, headache, restlessness, ataxia, confusion, seizures, urticaria	O, D
Dipyridil (herbicide)	Paraquat, diquat	Mucous membrane and airway irritation, abdominal pain, diarrhea, vomiting, gastrointestinal bleeding, pulmonary oedema, dermatitis, renal and hepatic damage, coma, seizures	O, D (via broken skin)
Fluoroacetate (rodenticide)	Sodium fluoroacetate	Vomiting, paresthesias, tremors, seizures, hallucinations, coma, confusion, arrhythmias, hypertension, cardiac failure	O, D (possible)
Halocarbons (fumigant)	Cellfume, Methyl bromide	Skin/airway/mucous membrane irritant, cough, renal dysfunction, confusion, seizures, coma, pulmonary oedema	O, R, D

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Mercury, organic (fungicide)	Methyl mercury	Metallic taste, paresthesias, tremor, headache, weakness, delirium, ataxia, visual changes, dermatitis, renal dysfunction	O, R, D
Metal phosphides (rodenticide, fumigant)	Zinc-, aluminium-, magnesium- phosphide	Abdominal pain, diarrhea, acidosis, shock, jaundice, paresthesias, ataxia, tremors, coma, pulmonary oedema, tetany, dermal irritation	O, R, D
Nitrophenolic and nitrocresolic herbicides	Dinitrophenol, dinitrocresol, dinoseb, dinosarn	Sweating, fever, confusion, malaise, restlessness, tachycardia, yellow skin staining, seizures, coma, renal insufficiency, hepatic damage	O, R, D
Chemical/ chemical class	**Examples of pesticides**	**Clinical presentation**	**Route of exposure[b]**
Organochlorines (insecticide)	Aldrin, dieldrin HCB, endrin, lindane	Cyanosis, excitability, dizziness, headache, restlessness, tremors, convulsions, coma, paresthesias, nausea, vomiting, confusion, tremor, cardiac arrhythmias, acidosis	O, R, D
Organophosphates (insecticides)	Malathion, parathion, dichlorvos, chlorpyrifos	Headache, dizziness, bradycardia, weakness, anxiety, excessive sweating, fasciculations, vomiting, diarrhea, abdominal cramps, dyspnea, miosis, paralysis, salivation, tearing, ataxia, pulmonary oedema, confusion, acetylcholinesterase inhibition	O, D
Organotin (fungicide)	Fentin acetate, fentin chloride	Airway, skin, and mucous membrane irritation, dermatitis, salivation, delirium, headache, vomiting, dizziness	O, R, D
Phenol derivatives (Fungicide, wood preservative)	Pentachlorophenol, dinitrophenol	Skin, airway, and mucous membrane irritation, contact dermatitis, dyspnea, diaphoreses, urticaria, tachycardia, headache, abdominal pain, fever, tremor	O, R, D
Phosphonates (herbicide)	Roundup, glyphosate	Airway, skin, and mucous membrane irritation, abdominal, pain, nausea, vomiting, shock, dyspnea, respiratory failure	O, R
Pyrethrins, Pyrethroids	Allethrin, cyfluthrin, permethrin	Allergic reactions, anaphylaxis, dermatitis, paresthesias, wheezing, seizures, coma, pulmonary oedema, diarrhea, abdominal pain	R, D
Strychnine (rodenticide)	Strychnine	Muscle rigidity, opisthotonus, rhabdomyolysis	O
Thallium (rodenticide)	Thallium sulfate	Abdominal pain, nausea, vomiting, bloody diarrhea, headache, weakness, liver injury, hair loss, paresthesias, neuropathy, encephalopathy, cardiac failure	O
Triazines (herbicide)	Atrazine, prometryn	Mucous membrane, ocular and dermal irritation	O, R, D

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CCA, chromated copper arsenate; HCB, hexachlorobenzene; MCPP, methyl chlorphenoxy propionic acid.

[a] This list is an overview and is not meant to be a comprehensive list of all pesticide and pesticide classes. The health worker is encouraged to use other resources and clinical experience in establishing health effect and causality for acute pesticide poisoning. Suggested online references include: http://www.who.int/whopes/recommendations/IPCSPesticide_ok.pdf, http://npic.orst.edu/npicfact.htm, http://www.epa.gov/pesticides/safety/healthcare/handbook/handbook.pdf, http://www.cdc.gov/niosh/topics/pesticides/pdfs/pest-cd2app2v2.pdf, http://hazard.com/msds/, http://www.epa.gov/pesticides/reregistration/status.htm, http://pesticideinfo.org/, http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB, http://www.pesticideinfo.org/Search_Countries.jsp.

[b] Route of exposure key: O, oral/ingestion; R, respiratory/inhalation; D, dermal or ocular.

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Table 2: Definition of residues for enforcement and dietary exposure assessment (FAO, 1998, 1999a,b,c, 2000).

Pesticide (commodity)	**Checking compliance with MRL**[a]	**Dietary exposure assessment**
Bitertanol (plant)	Bitertanol	Bitertanol
Bitertanol (animal)	Bitertanol	Sum of bitertanol, *p*-hydroxybitertanol and acid-hydrolysable conjugates of *p*-hydroxybitertanol
Carbofuran (plant)	Sum of carbofuran and 3-hydroxy carbofuran expressed as carbofuran	Sum of carbofuran and 3-hydroxy carbofuran, free and conjugated, expressed as carbofuran
Chlorothalonil (plant)	Chlorothalonil	Chlorothalonil
Chlorothalonil (animal)	Chlorothalonil	Sum of chlorothalonil and 4-hydroxy-2,5,6-trichloroisophthalonitrile, expressed as chlorothalonil
Fenpropimorph (plant)	Fenpropimorph	Fenpropimorph
Fenpropimorph (animal)	2-Methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]} propionic acid expressed as fenpropimorph	
Glyphosate (plant)	Glyphosate	Sum of glyphosate and aminomethylphosphonic acid, expressed as glyphosate
Kresoxim-methyl (plant)	Kresoxim-methyl	Kresoxim-methyl
Kresoxim-methyl (animal)	*α*-(*p*-Hydroxy-*o*-tolyloxy)-o-tolyl(methoxyimino) acetic acid, expressed as kresoxim-methyl	
Quintozene (plant)	Quintozene	Sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulphide, expressed as quintozene
Quintozene (animal)	Sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulphide, expressed as quintozene	
Thiabendazole (plant)	Thiabendazole	Thiabendazole
Thiabendazole (animal)	Sum of thiabendazole and 5-hydroxy thiabendazole	Sum of thiabendazole, 5-hydroxy thiabendazole and 5-hydroxy thiabendazole sulfate

[a]MRL, maximum reside limit.

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Table 3: Literature review on biotransformation of pesticides with fermentation and their effects on foods quality and safety in the last 20 years.

Food	**Pesticides**	**Pesticides losses and metabolites**	**Fermentation defects**	**Quality and safety effects**	**References**
Bread	endosulfan, hexaconazole, propiaconazole, malathion, chlorpyriphos, deltamethrin	endosulfan (70%) deltamethrin (63%) malathion (60%) propiaconazole (52%) chlorpyriphos (51%) hexaconazole (46%)	endosulfan, hexaconazole and propiaconazole suppressed the growth of the yeast in the range 7.5–33.5%, 12.5–44.7% and 11–40%, respectively	endosulfan, hexaconazole and propiaconazole affect the sensorial quality of the bread	Sharma et al. (2005)
Cheese	DDT	the reduction of DDT in Ras cheese made from contaminated milk (0.1-10.0 mg/kg fat) were 25.5-40.6%, at the end of storage	The addition of 1.0 mg/kg (the maximum permissible level for dairy products by FAO/WHO, 1993) did not affect the growth of microorganisms during the incubation	the isolated Ras cheese microorganisms reduced DDT by 10.8, 11.8 and 4.8% for *Streptococci*, *Lactobacilli* and yeasts, respectively, what makes Ras cheese safer	Abou-Arab (1997)
Kimchi (fermented Chinese cabbage)	cadusafos chlorpyrifos coumaphos diazinon dyfonate ethoprophos fenamiphos methylparathion parathion	cadusafos (10-20%) chlorpyrifos (10-80%) coumaphos (10-40%) diazinon (10-80%) dyfonate (10-30%) ethoprophos (5-15%) fenamiphos (5-50%) methylparathion (10-80%) parathion (10-80%)	the four strains grew well until day 1, decreased slowly by day 2, and then increased gradually at day 6	the fermented kimchi meets the minimal residue criteria for food safety due to OP degradation by kimchi microorganisms	Cho et al. (2009)
Kimchi (fermented Chinese cabbage)	lufenuron	the dissipation of lufenuron followed monophasic first order kinetics showing varying degradation throughout the 10-day periods with half-lives of 4.6-5.8 days	the deposited level on Chinese cabbage under greenhouse conditions seemed to be difficult to produce the crop with 0.2 mg/kg of MRL of the Korea Food and Drug Administration (KFDA)	the monitoring and surveillance of the terminal residue level is crucial to food safety	Khay et al. (2008)

(a) Solid foods:

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Food	Pesticides	Pesticides losses and metabolites	Fermentation defects	Quality and safety effects	References
Fermented sausage	DDT lindane	DDT (10%) -> DDD Lindane (18%) -> 2,4-, 2,5-, 2,6- and 3,4-dichlorophenol; 2,3,4- and 2,3,5-trichlorophenol; hexachlorobenzene; and pentachlorophenol	slight decrease in counts of the strains during the initial incubation; then the microorganisms recovered and began to grow logarithmically, but not as well as in a normal situation	degradation activity of *M. varians* could be of great value for detoxifying OCPs contamination that occurs in foods of animal origin	Abou-Arab (2002)
Fermented green table olive	kaolin and copper based products	no data	lactic acid bacteria population was affected by both treatments, especially by copper, while yeasts were affected only partially by copper at the beginning of fermentation, and after 180 days at a constant concentration till the end of the process	samples treated both with kaolin and copper based products exhibited higher values in saltiness, bitterness, acidity, hardness and fibrousness descriptors	Randazzo et al. (2011)
Fermented tea	imidacloprid acetamiprid	imidacloprid (20-25%) acetamiprid (15-20%)	maximum loss was during withering and drying (65-70%), while rolling and fermentation do not have much impact	overboiling the tea leaves might be the chance of more transfer of pesticides from made tea to infusion	Gupta and Shanker (2009)
Fermented tea	dimethoate, quinalphos, dicofol, deltamethrin	no losses	rolling and fermentation in black tea manufacturing did not contribute to any significant decrease in pesticide level	no effects	Sood et al. (2004)

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(b) Liquid foods:

Food	**Pesticides**	**Pesticides losses and metabolites**	**Fermentation defects**	**Quality and safety effects**	**References**
Beer	myclobutanil, propiconazole, nuarimol	propiconazole (47%) myclobutanil and nuarimol (~20%)	after 3 days, sluggish fermentation after 8 days, stuck fermentation (the three compounds are systemic fungicides, and interfere with ergosterol biosynthesis by inhibiting the demethylation of steroids)	if pesticide residues are present in the fermenting wort, they may cause organoleptic alterations to the finished beer and have toxic effects for the consumer	Navarro et al. (2005)
Beer	>300 pesticides	the only pesticide for which the degradation ratio was 20% is methamidophos, and 16 other were degraded at <50%	these pesticides that had low log P values, being <2 (with hydrophilic properties), and also high thermal stability largely affect brewing	pesticides remaining in beer can cause sensorial defects	Inoue et al. (2011)
Beer	chlorfenapyr, quinoxyfen, tebuconazole, fenarimol, pyridaben, dimethomorph	dimethomorph was the only remaining into the beer at an appreciable level	polar compounds at large concentrations can affect brewing	potential risk of pesticide exposure from the consumption of beer produced with the agrochemicals studied is low	Hengel and Shibamoto (2002)
Beer	pendimethalin, trifluralin fenitrothion, malathion, methidathion	strongly depend on their log K_{OW}	the fermentation kinetic was sluggish for the samples treated with fenitrothion, malathion, and trifluralin. but increased from the second to the sixth day in the methidathion and pendimethalin treatments	higher amount of residual sugars, differences in pH and color of the beer, and lower total polyphenol content after sluggish fermentation	Navarro et al. (2007)

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Food	**Pesticides**	**Pesticides losses and metabolites**	**Fermentation defects**	**Quality and safety effects**	**References**
Fermented milk	lindane	reduction of lindane was 1.4-8.9% during the manufacture and storage of yoghourt for 3 days in a refrigerator	no data	although the levels of lindane were reduced, other < were detected (namely 2,6-dichlorophenol, 2,3,4-trichlorophenol and 2,5-dichlorophenol), which can be more toxic than lindane	Abou-Arab (1999b)
Fermented milk	anadol (fungicide) tasolen (fungicide) round up (herbicide) saturn (herbicide) lannate (insecticide) reldan (insecticide)	All pesticides experimented a degradation of 40-50% after 10 h of fermentation	*Bifidobacterium* spp. 420 was the most sensitive to fungicides anadol and tasolen *St. thermophilus* was the most sensitive for herbicides *Bifidobacteria* spp. exhibited excessive sensitivity toward insecticides	Insecticides (lannate and reldan) delayed the acid production by yoghourt culture more than herbicides and fungicides. Acetaldehyde and diacetyl decreased with increasing of pesticides	Abou-Ayana et al. (2011)
Fermented milk	dimethoate, fenthion, malathion, methyl parathion, monocrotophos, phorate, trichlorphon	starter from Rhodia accelerated degradation of methyl parathion, monocrotophos and phorate, but the starter from Danisco had no impact. Degradation of dimethoate, fenthion and trichlorphon during yoghurt processing increased for both starters	the microbial cultures of the commercial starters were tolerant to the added pesticides	There was no effect of presence of organophosphorus pesticides on yoghurt formation from bovine milk.	Bo et al. (2011)
Fermented milk	denthion, dimethoate, malathion, methyl parathion, monocrotophos, phorate, and trichlorphon	degradation of methyl parathion, trichlorfon, phorate, denthion and dimethoate in the fermented with Rhodia starter had an increase of 26, 24, 20, 14 and 12%, respectively	no data	lactic acid fermentation could reduce the level of organophosphorus pesticide in dairy products, and decrease the safety risk of the products	Bo and Zhao (2010)

Food	Pesticides	Pesticides losses and metabolites	Fermentation defects	Quality and safety effects	References
Vinegar	pyrimethanil, flufenoxuron, chlorpyrifos-methyl, vinclozolin, metalaxyl, fenitrothion, malathion, dicofol, chlorpyrifos, cyprodinil, triadimenol, procymidone, hexythiazox, folpet, fludioxonil, iprodion, benalaxyl, fenhexamid	most of them decrease during the period of ripening. Chlorpyrifos and folpet disappeared with the beginning of alcoholic fermentation, whereas triadimenol was completely degraded during fermentation. Metalaxyl decreased but did not disappear, ranging from 7.8 to 3.8 µg/L. Metalaxil did not disappear with the acetic fermentation, finding lower values of 3.7-1.9 µg/L.	no data	Metalaxyl presents a high persistence, but the found values are low enough to consume this product without any kind of health risk.	Durán-Guerrero et al. (2009)
Wine	pyrimethanil	no data	pyrimethanil had an effect on the course and successful conclusion of spontaneous wine fermentation that was correlated with the initial concentration of yeasts in the must.	below maximum residue limits, the utilization of sugar and concentration of yeast cells in the start of the spontaneous fermentation were influenced by pyrimethanil.	Cus and Raspor (2008)
Wine	dichlofluanid, benomyl, iprodione, procymidone, vinclozolin	dichlofluanid (100%), benomyl (0%), Iprodione (70-80%), procymidone (70-80%), Vinclozolin (100%)	tested fungicides had a negative effect on in vitro yeast growth, especially dichlofluanid and benomyl. *Zygosaccharomyces rouxii* and *Saccharomyces cerevisiae* were the most resistant yeasts while *Rhodotorula glutinis* was the most susceptible.	wine samples had unaltered physical, chemical and organoleptic properties, though with benomyl a slight delay in the initiation of fermentation process was observed	Calhelha et al. (2006)
Wine	famoxadone	famoxadone (>90%)	during the wine-making process, it is mostly adsorbed in the cake and lees.	no effects	De Melo-Abreu et al. (2006)

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Food	**Pesticides**	**Pesticides losses and metabolites**	**Fermentation defects**	**Quality and safety effects**	**References**
Wine	zoxamide	*Kloeckera apiculata* was more effective compared to *Saccharomyces cerevisiae* in decreasing residues levels at higher levels of zoxamide, 43 *vs.* 35%. Malolactic fermentation of *Oenococcus oeni* lactic bacteria did not affect zoxamide.	zoxamide did not affect the alcoholic and malolactic fermentation processes.	no effects	Angioni et al. (2005)
Wine	carbendazim, chlorothalonil, fenarimol, metalaxyl, oxadixyl, procymidone, triadimenol carbaryl, chlorpyrifos, dicofol	after malolactic fermentation using *Oenococcus oeni*, the concentrations of the active compounds chlorpyrifos (70%) and dicofol (30-40%) were the most significantly reduced.	dicofol had a major inhibitory effect on the catabolism of malic acid (only 6-13% was metabolized), whereas chlorothalonil, chlorpyrifos, and fenarimol had only a minor effect (76-84% was metabolized).	In the case of dicofol, a substantial slowing of malolactic fermentation was observed when this compound was present at high concentration	Ruediger et al. (2005)
Wine	cyprodinil, fludioxonil, pyrimethanil, quinoxyfen	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.	no data	fungicide dissipation curves is a valuable tool to ascertain the evolution of different active ingredients during the conversion of grapes to must and that of must to wine, and discuss which MRL should be established by law for wine. The winemaker can also choose which winemaking process to follow depending on the residues.	Fernandez et al. (2005)

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Food	**Pesticides**	**Pesticides losses and metabolites**	**Fermentation defects**	**Quality and safety effects**	**References**
Wine	captan	captan degraded 100% to tetrahydrophthalimide (THPI) at the end of fermentation.	the metabolite was present at low levels on grapes, and, unlike captan, it had no negative effect on the fermentative process.	THPI is very stable, and after 1 year, its concentration was unchanged. Therefore, its determination in wine should be considered.	Angioni et al. (2003)
Wine	quinoxyfen	at the end of fermentation with and without maceration no quinoxyfen was determinable in the wine.	no effect on the alcoholic or malolactic fermentation was observed even in the presence of high quinoxyfen concentrations.	no effects	Cabras et al. (2000)
Wine	review on the results obtained in the 1990s from research on the behavior of pesticide residues on grapes and their fate in wine-making	pesticide residues in wine were always smaller than on the grapes, except for those that did not have a preferential partition between liquid and solid phase (azoxystrobin, dimethoate, and pyrimethanil)	the new fungicides have shown no effect on alcoholic or malolactic fermentation. In some cases the presence of pesticides has also stimulated the yeasts, especially *Kloeckera apiculata*, to produce more alcohol.	only for those stimulating the yeasts	Cabras and Angioni (2000)
Wine	azoxystrobin, cyprodinil, fludioxonil, mepanipyrim, pyrimethanil, tetraconazole	alcoholic fermentation did not affect the amount of pesticides either by degradation or by adsorption. The bacteria studied did not show too a degradative effect on pesticides during malolactic fermentation.	their presence stimulated the yeasts, especially *K. apiculata*, to produce more alcohol. During malolactic fermentation by *Le. oenos*, malic acid decreased slightly less (by ~15%) in the presence of all pesticides, except mepanipyrim. A lower effect (~5%) was found during the fermentative process with *L. plantarum*.	little quality effects (more alcohol and less malic acid) were observed for the yeast *K. apiculata* and bacteria *Le. oenos*.	Cabras et al. (1999)

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Food	Pesticides	Pesticides losses and metabolites	Fermentation defects	Quality and safety effects	References
Wine	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 data	no risks of quality and safety deffects	Angioni et al. (2011)
Wine	117 pesticides	they significantly diminished through vinification, particularly the pressing of crushed grapes and wine racking after alcoholic fermentation. The pesticides detected in wine were boscalid, cyprodinil, dimethomorph, fenhexamid, metalaxyl and procymidone	no data	no risks of quality and safety defects	Cus et al. (2010a)
Wine	fenamidone, pyraclostrobin, trifloxystrobin	After winemaking, fenamidone, pyraclostrobin, and trifloxystrobin were not detected in the wine, but they were present in the cake and lees. This was due to the adsorption of pesticide residues to the solid parts	no data	These three active ingredients could be used in a planning to obtain residue-free wines	Garau et al. (2009)
Wine	chlorpyrifos, penconazole, fenarimol, vinclozolin, metalaxyl, mancozeb	chlorpyrifos (100%), penconazole (95%), fenarimol (93%), vinclozolin (95%), metalaxyl (60%), mancozeb (100%)	no data	only the very hydro-soluble metalaxyl significantly remains in the wine	Navarro et al. (1999)

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Food	Pesticides	Pesticides losses and metabolites	Fermentation defects	Quality and safety effects	References
Wine	metalaxyl, lindane, fenvalerate, deltamethrin	the pyrethroids, fenvalerate and deltamethrin, do not persist in the experimental wines, while lindane (60-90%) and metalaxyl (80%) are found in relatively high concentrations	no data	Compounds related to the 2,6-dimethylaniline moiety for metalaxyl, isomerization and dehydrochlorination products for lindane, and hydrolysis derivatives of the pyrethroids appear to be the degradation products found in must and wine extracts too	Jiménez et al. (2007)
Wine	copper, dichlofluanid	uptake by *Oe. oeni* was also studied, and it was found that very small quantities were retained by resting cells at pH 6 but that this amount decreased significantly at pH 3.5 or when substrates such as glucose, fructose, or L-malic acid were available for cells.	minimal inhibitory concentrations that affected malolactic fermentation were just under 5 mg/L, which was enhanced by ethanol.	no effects	Vidal et al. (2001)
Wine	famoxadone, fenhexamid, fluquinconazole, kresoxim-methyl, quinoxyfen, trifloxystrobin	no data	during the wine-making process, there was no adverse effect of the pesticides on the yeast count even in the grapes treated on the day of harvest	no effects	Oliva et al. (2007)
Wine	quinoxyfen	79–82% fungicide removal by alcoholic fermentation	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,	quinoxyfen led to significantly lower ethylic ester levels. Fusel alcohol synthesis and volatile acid levels did not present a uniform trend in relation	Sarris et al. (2009)

			observed when the quinoxyfen concentration was increased.	with the added fungicide.	

Food	**Pesticides**	**Pesticides losses and metabolites**	**Fermentation defects**	**Quality and safety effects**	**References**
Wine	tebuconazole	87% losses and no metabolites	no effect on the alcoholic or malolactic fermentation was observed	no data	González-Rodríguez et al. (2009b)
Wine	boscalid, fenhexamid, cyprodinil, dimethomorph, fludioxonil, metalaxyl, procymidone, azoxystrobin, iprodione	the combined fining agent containing bentonite, potassium caseinate, polyvinylpolypyrrolidone and diatomaceous earth was more efficient in lowering the concentration of boscalid in wine if compared with bentonite.	no data	the results of microbiological quality indicate that no less than one quarter of bottled wines on our store shelves is microbiologically unstable.	Cus et al. (2010b)
Wine	cyprodinil, fludioxonil, pyrimethanil	no data	assays inoculated with *S. cerevisiae* (*syn. bayanus*) behave significantly different with the addition of fungicides	The lower quality wines, according to isomeric alcohol content are those obtained by inoculation with *S. cerevisiae* (*syn. bayanus*) and addition of cyprodinil. Fungicides in the assays inoculated with *S. cerevisiae* (*syn. bayanus*) also produces an increase in the ethyl acetate and isoamyl acetate contents, which causes a decrease in the sensorial quality of the wine obtained.	García et al. (2004)
Wine	fenoxaprop-P-ethyl, tribenuron methyl, glyphosate	no data	while pure active compounds affect cell growth and metabolism at a lower extent, commercial preparations have a significant major negative influence on	the supplementation with the highest concentration of glyphosate was able to induce the assimilation and	Braconi et al. (2006)

			yeast biology.	oxidation of several carbon sources and to greatly increase the overall metabolic activity	

Food	Pesticides	Pesticides losses and metabolites	Fermentation defects	Quality and safety effects	References
Wine	pyraclostrobin, famoxadone, benalaxyl-M, iprovalicarb, benalaxyl	dissipation of fungicide residues in high percentages (~95%), except for iprovalicarb (75%)	no data	estimated MRLs for white wines were proposed for future EU legislation to control the presence of pesticides in white wines	González-Rodríguez et al. (2009a)
Wine	flusilazole	no data	the plasma membrane fluidity was altered by the presence of methyl sterol which increased with flusilazole concentration	the short free fatty acids (C6 to C14) and the unsaturated free fatty acids increased in the cells, while the short free fatty acids decreased in the medium	Doignon and Rozes (1992)
Wine	cyazofamid, famoxadone, mandipropamid, valifenalate	dissipation of fungicide residues in high percentages (~95%), except for valifenalate (70%)	no data	estimated MRLs for white wines were proposed for future EU legislation to control the presence of pesticides in white wines	González-Rodríguez et al. (2011a)
Wine	benalaxyl, iprovalicarb, pyraclostrobin	no data	no data	reduced the varietal aroma of wines attributed to geraniol. Increase in the fruity aroma due to several ethyl esters and acetates	González-Rodríguez et al. (2011b)
Wine	tebuconazole	no data	no data	terpene and higher-alcohol concentrations were essentially not changed; by contrast, C6-alcohol, ester and aldehyde concentrations differed significantly.	Noguerol-Pato et al. (2011)

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Table 4: Principal compounds responsible for wine aroma.

Class	Compound	Concentration in wine (mg/L)	Aroma
Carbonyl compounds	Acetaldehyde	10-300	Bitter, green pineapple
	Benzaldehyde	0.003-4.1	Bitter almond
	Diacetyl	0.05-5	Larder
Esters	Ethyl acetate	26-180	Varnish, nail polish, fruity
	Ethyl butanoate	0.01-1.8	Floral, fruity
	Ethyl decanoate	Trace to 2.1	Floral
	Ethyl hexanoate	Trace to 3.4	Apple, banana, violet
	Ethyl octanoate	0.05-3.8	Pineapple, pear
	Isoamyl acetate	0.03-8.1	Banana, pear
	Isobutyl acetate	0.01-0.8	Banana
	2-Phenylethyl acetate	0.01-4.5	Rose, honey, fruity, floral
Higher alcohols	Butanol	0.5-85	Petrol
	Hexanol	0.3-12	Freshly mown grass
	Isoamyl alcohol	45-490	Marzipan
	Isobutylic acid	9-28	Alcoholic
	2-Methyl-1-butanol	15-150	Marzipan
	2-Phenylethanol	10-180	Floral, rose
	Propanol	9-68	Powerful
Volatile fatty acids	Acetic acid	150-900	Vinegar
	Butyric acid	Trace	Bitter
	Decanoic acid	Trace to 54	Unpleasant, rancid, bitter, phenolic
	Hexanoic acid	Trace to 37	Rancid, vinegar, cheese
	Octanoic acid	Trace to 41	Oily, rancid, sweet, buttery
	Propionic acid	Trace	Rancid
Volatile phenols	4-Ethyl guaiacol	0-1.561	Smoky, vanilla
	4-Ethylphenol	0-6.047	Horse sweat

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	4-Vinyl guaiacol	0-0.496	Smoky, vanilla
	4-Vinylphenol	0-1.15	Medicinal
Sulfur compounds	Dimethyl disulfide	Trace to 0.0016	Boiled cabbage
	Diethyl disulfide	Trace	Garlic, burnt rubber
	Ethyl mercaptan	Qualitative	Onion, rubber
	Hydrogen sulfide	Trace to 0.080	Rotten eggs
	Methyl mercaptan	Qualitative	Rotten eggs, cabbage

Data taken from Cabanis et al. (1998), and Lambrechts and Pretorius (2000).

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