Food processing as a means for pesticide residue dissipation

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SUMMARY

Pesticides are one of the major inputs used for increasing agricultural productivity of crops. However, their inadequate application may produce large quantities of residues in the environment and, once the environment is contaminated with pesticides, they may easily enter into the human food chain through plants, creating a potentially serious health hazard. Nowadays, consumers are becoming more aware of the importance of safe and high quality food products. Thus it is pertinent to explore simple, cost-effective strategies for decontaminating food from pesticides. Various food processing techniques, at industrial and/or domestical level, have been found to significantly reduce the contents of pesticide residues in most food materials. The extent of reduction varies with the nature of pesticides, type of commodity and processing steps. Pesticides, especially those with limited movement and penetration ability, can be removed with reasonable efficiency by washing, and the effectiveness of washing depends on pesticide solubility in water or in different chemical solvents. Peeling of fruit and vegetable skin can dislodge pesticide residues to varying degrees, depending on constitution of a commodity, chemical nature of the pesticide and environmental conditions. Different heat treatments (drying, pasteurization, sterilization, blanching, steaming, boiling, cooking, frying or roasting) during various food preparation and preservation processes can cause losses of pesticide residues through evaporation, co-distillation and/or thermal degradation. Product manufactures, from the simplest grain milling, through oil extraction and processing, juicing/pureeing or canning of fruits and vegetables, to complex bakery and dairy production, malting and brewing, wine making and various fermentation processes, play a role in the reduction of pesticide contents, whereby each operation involved during processing usually adds to a cumulative effect of reduction of pesticides present in the material. There is diversified information available in literature on the effect of food processing on pesticide residues which has been compiled in this article.

Keywords: Pesticides; Residues; Food processing
INTRODUCTION

Food is the basic necessity of life, and nowadays, in the era of rapid population growth coupled with limited expansion of cultivated land area, the required increase in food productivity is focused mainly on yield rise. It is ensured through intensive usage of pesticides, which contribute to good yield and satisfactory harvest with minimal losses during storage. Due to the extensiveness of current applications of pesticides in agriculture against pre- and postharvest pests, regardless of the effectiveness of those agrochemicals, especially novel ones, still a very small fraction of applied pesticides end up being directly involved in the pesticidal mechanism, while most of the active ingredients find their way into the environment as residues. Once the environment becomes contaminated with pesticides, they may easily enter the human food chain through plants, creating serious acute health hazards. Pesticides have high toxicity, and their toxic effects on humans are recognized as either acute or chronic, the latter resulting from a long-term exposure to low doses or regular intake of pesticide residues from food. The use of pesticides in crops and the levels of residues in food have been regulated worldwide and the correct use of pesticides does not cause problems of public concern in the area of human health and environmental safety. However, if inappropriate abusive treatments are applied without respecting safety recommendations, undesirable residues can remain on agricultural products and can be transferred to food. In the light of increasing reports on pesticide contamination of food commodities, consumers and buyers are becoming more aware of the importance of safe and high quality food products. Thus it is prudent to explore simple, cost-effective strategies that address this situation of food safety. Food processing at domestic and industrial level would offer a suitable means to tackle the current scenario of unsafe food.

As various food commodities, as well as pesticides applied to those commodities, differ in composition and properties, according to their nature and chemical class, there are numerous factors that affect the extent of pesticide absorbance, penetration and degradation, and those differ from one category of food to another. Whether pesticides will remain on food/crop surface after application or will be absorbed into it highly depends on the physicochemical properties of pesticide molecules, as well as the food/crop itself. If most of a pesticide remains on plant surface, most of it can be removed by simple washing and/or peeling, or by treatments with different chemical solutions. However, when pesticides penetrate into food commodities, the location of their residues depends mainly on their partitioning properties, i.e. their water solubility, while the rate at which pesticides move through food/crops is closely related to all physicochemical parameters of the pesticides, as well as the surrounding environment. Knowing those parameters is crucial in a search for effective methods to remove residues from products.

Usually, primary food commodities are subjected to various processing operations prior to their release onto the market. The processing of food commodities generally implies a transformation of the perishable raw commodity into a value added product that has greater shelf life and is closer to be table ready. Food processing techniques include all processes that in some way lead to transformation of raw materials into food, whether they involve a multistep and complex processing at the industry level, or simple domestic processing. The mechanisms leading to changes in pesticide residue levels during processing are: thermal degradation (decomposition), dissolving, hydrolysis, oxidation and reduction, photolysis, volatilization, enzymatic transformation due to microbial degradation, changes in pesticide residue levels due to weight changes and changes in pesticide residue levels due to the partitioning properties of the pesticides. Various techniques and methods involved during processing at the industrial or domestic levels usually play a role in the pesticides reduction process, whereby each operation has a cumulative effect on the reduction of pesticides present. However, some processes may lead to increased residue levels due to concentration effect and/or affinity to lipid moiety. Therefore, it is of great interest to gather information about the effects of different food processing techniques on the fate of pesticide residues in food.

EFFECTS OF PREPARATORY STEPS ON PESTICIDE RESIDUE DISSIPATION

Washing with water

As most fruits, vegetables and leafy commodities used for food undergo the washing step prior to consumption or further processing, it could be expected for pesticides, especially those with limited movement and penetration ability and with a high tendency of loosely maintaining at outer surface, to be removed with reasonable efficiency by this preparatory step. The effectiveness of washing depends on pesticide solubility in water or in different chemical solvents.

The idea of removing pesticides from food by simple washing occurred very early. Depending on the constitution of each food commodity, chemical nature
of pesticides and environmental conditions, the reported rates of residue reduction have varied significantly. Yoshida et al. (1992) reported that the removal rates of dieldrin and heptachlor epoxide were up to 52 and 67% in pumpkins and cucumbers, respectively, while another report showed that washing removed more residues from carrot than from tomatoes (Burchat et al., 1998). Abou-Arab (1999) reported losses of HCB, p,p'-DDT, lindane, pirimiphos-methyl, dimethoate and profenofos (9.17-22.7%) after tomatoes were washed with tap water. Furthermore, residues of bifenthrin, chlorothalonil, chlorpyrifos, cypermethrin, dimethoate, lindane, malathion, mancozeb, maneb, methyl-parathion, oxadixyl, procimidone, propineb, thiophanate-methyl and λ-cyhalothrin were successfully removed from tomatoes, either entirely or to significant levels, by simple washing with tap water (Chavarri et al., 2004, 2005; Cengiz et al., 2007; Rani et al., 2013; Chauhan et al., 2012, 2012a; Kwon et al., 2015; Reiler et al., 2015). According to data published over the past years, it seems that a general correlation between the rinsing ability of a pesticide and its water solubility exists, but some pesticides have demonstrated specific behaviour. Kumar and Agarwal (1991) reported 77.8% reduction in dithionin residues, and Vijayasee et al. (2015) 86.38-88.78% reduction of chlorantraniliprole residues in eggplant after washing. Similar results were obtained by Randhawa et al. (2007), who recorded a significant reduction of chlorpyrifos and its degradation products after washing of eggplant, tomato, okra, spinach, cauliflower and potato. In cabbage, washing with tap water provided the least effective, while still significant, reduction (approx. 15-19%) of chlorpyrifos, p,p'-DDT, cypermethrin and chlorothalonil, compared with washing in different solutions (Zhang et al., 2007). In cucumbers, the initial diazinon residue level decreased by 22.3% after rubbing for 15 s under running water (Cengiz et al., 2006), similar to the 23% carbaryl residue dissipation after washing (Hassanzadeh et al., 2010). The reported results were in agreement with data reported by Liang et al. (2012), who found that cucumber washing with tap water for 20 min provided a significant reduction of trichlorfon, dimethoate, dichlorvos, fenithrothion and chlorpyrifos of up to 53.7, 32.6, 52.4, 26.7 and 62.9%, respectively. The level of chlorpyrifos in asparagus dropped by 24% after washing, while the procedure entirely removed mancozeb, maneb and propineb (Chavarri et al., 2005), as well as azoxyystrobin (Yang et al., 2012) from spinach. Also, Łozowicka and Jankowska (2016) found that washing with tap water reduced 6-67% of malathion residues (Bhagirathi et al., 2001), the concentrations of chlorpyrifos and fenitrothion residues were 30-40% lower on red pepper after shaking or sonicating for 5 min in water (Lee, 2001), while the amount of pyridaben in hot pepper fruit after washing was reduced by >50% (Kim et al., 2015). Finally, washing of potatoes with tap water also lead to a reduction in pesticide residues levels: chlorpropham was thus reduced by 33–47% (Lentza-Rizos & Balokas, 2001), while lindane, aldrin and heptachlor epoxide decreased by 10-12% (Zohair, 2001). Soliman (2001) reported a somewhat higher reduction of lindane, up to 20.7% after potato washing, while HCB, p,p'-DDT, dimethoate, pirimiphos-methyl and malathion were reduced up to 27.7, 18.1, 12.4 18.1 and 11.2%, respectively. Tejada et al. (1990) and Lee et al. (1991) revealed that the usual practice of washing maize and rice before cooking could reduce chlorpyriphos and its breakdown product residues by 60-100%. Permethrin was almost completely removed from rice by washing in a study by Fukuhara et al. (1994), while Yang et al., (2012) reported a complete removal of propiconazole from white rice and a considerable reduction of iprobenfos and fenobucard by washing of white, coloured and unpolished rice, as well. Miyahara and Saito (1994) suggested that dichlorvos, malathion, chlorpyrifos and captan remained as micro-particles on the surface of soybeans after spraying, which is why they are easily removed (80-90%) by mechanical stirring in water.

Regarding fruits, the concentration of iprodione in peaches was reduced by >50% after washing (Lentza-Rizos, 1995), while this procedure led to considerable reductions (8-34%) of methidathion, iprodione, malathion, myclobutanil, parathion-methyl, chlorpyrifos, fenamidol and pirimicarb residues in nectarines (Pugliese et al., 2004). The effectiveness of washing with tap water resulted in 75% azoxyystrobin removal from grapes (Lentza-Rizos et al, 2006), as well as 20-68% reduction of bupirimate, pirimicarb, tetraconzole, deltamethrin, pyraclostrobin, λ-cyhalothrin, folpet, boscalid, iprodione, trifloxystrobin, fludioxonil, cyprodinil, α-cypermethrin, fenhexamid, acetamiprid and chlorpyrifos from strawberries (Łozowicka et al., 2016). Washing caused an important decrease in iprodione and phosalone contents but did not affect the levels of bitertanol and procymidone in prunes (Cabas et al., 1998). Washing of apples brought about 30-50% reduction in phosalone residues (Mergnat et al., 1995), 53% reduction in azinophos-methyl residues (Ong et al., 1996), 50% reduction in fenitrothion (Lipowska et al., 1998) and captan (Rawn et al., 2008), while Li et al. (2015) reported that intensive apple washing, as a first step in apple processing during juice production,
reduced the residues of chlorpyrifos, β-cypermethrin, tebuconazole, acetamiprid and carbendazim by 21.3, 6.2, 11.9, 66.2 and 47.3%, respectively.

**Washing with solutions**

Although washing with tap water has proved to be a significantly effective, simple, common and convenient method for removing pesticide contaminants from food surfaces, it has been shown that washing with dilute salt and/or chemical solutions can often be even more effective to this cause. Thus, decontamination of tomatoes by washing with different solutions showed that 10% acetic acid and 10% sodium chloride solutions gave 3-4 fold higher loss in HCB, lindane, p,p'-DDT, dimethoate, profenofos and pirimiphos-methyl, compared with tap water washing (Abou-Arab, 1999). Radwan et al. (2005) indicated that washing with acetic acid solution ensured a total removal of profenofos residues from eggplant and high percent removal from peppers. As Liang et al. (2012) reported, the highest loss of trichlorfon and dimethoate from cucumber was caused by washing in 5% sodium carbonate solution, while 5% sodium bicarbonate solution caused the highest reductions in dichlorvos, fenitrothion and chlorpyrifos. According to those authors, acetic acid solution was also suitable for removing dichlorvos. Acidic solutions were found to be more effective for elimination of organochlorine pesticides from potatoes, while organophosphorus pesticides were effectively eliminated with neutral and alkaline solutions (Zohair, 2001). Soliman (2001) confirmed that washing with 10% acetic acid solution led to somewhat higher removal of HCB, lindane, p,p'-DDT, dimethoate, pirimiphos-methyl and malathion from potatoes, compared with 10% sodium chloride solution, while both solutions were more effective than washing with tap water. Zhang et al. (2007) reported that washing with 10% acetic acid and 10% sodium chloride solutions caused at least a 3-fold higher removal of chlorpyrifos, p,p'-DDT, cypermethrin and chlorothalonil from cabbage compared with water washing, while acetic acid was more effective than sodium chloride only for chlorpyrifos removal. The results of washing green chillies with salt water did not differ significantly from ordinary washing with tap water but their dipping in 2% sodium chloride solution for 10 minutes removed higher amounts of triazophos and acephate residues (Phani-Kumar et al., 2000). Solutions of common salt (2%) and slaked lime (2%) were more effective than tap water in chlorantraniliprole removal from eggplant, while the same pesticide was also effectively removed from okra fruits with vinegar 2% and turmeric 1% solutions (Vijayasekhar et al., 2015). Kim et al. (2000) treated soybeans with 0.3 ppm ozone water for 30 minutes and the residues of diazinon, dichlorvos and chlorpyrifos were destroyed with higher efficiency than by washing with pure water. Ozonized water was also effective in removing diazinon, parathion and methyl-parathion from vegetables, whereby the efficacy highly depended on the dissolved ozone levels (Wu et al., 2007). Similarly, Łozowicka and Jankowska (2016) reported higher reduction of cyprodinil and pyraclostrobin from tomatoes and α-cypermethrin, azoxystrobin, boscalid, chlorpyrifos, λ-cyhalothrin and pyraclostrobin from broccoli after washing with ozonized, compared to tap water. Washing with ethanol removed chlorpyrifos, fenarimol, iprodione, malathion, methidathion, myclobutanil, parathion methyl and pirimicarb from nectarines at the highest rates, while washing with sodium laurylsulfate and glycerol were second and third most effective methods (Pugliese et al., 2004). The authors concluded that the effectiveness of the tested washing solutions seemed to be related with the solubility of pesticides in them. As all pesticides have high solubility in ethanol, it was resultingly found very effective. On the other hand, sodium laurylsulfate forms molecular micelles which allow the residues of pesticides with high hydrophobicity and low water solubility (e.g. chlorpyrifos) to be adsorbed, and this explains the washing efficiency of that solvent. Lower efficiency of glycerol is probably due to its higher viscosity. Hwang et al. (2001) reported that mancozeb residues decreased at the highest rate on apples after chlorine and chlorine-dioxide treatments, followed by ozone and peroxyacetic acid treatments. Hadzhikinova et al. (2006) reported that washing with sodium base (1%) or sodium hydrogen carbonate (1.5%) solutions reduced concentrations of chlorpyrifos-methyl and fenarimol in cherries, while Łozowicka et al. (2016) found that washing with ozone water was more effective than tap water in removal of bupirimate, primicarb, tetraconzole, deltamethrin, pyraclostrobin, λ-cyhalothrin, folpet, boscalid, iprodione, trifloxystrobin, fluoioxonil, cyprodinil, α-cypermethrin, fenhexamid, acetamiprid, and chlorpyrifos from strawberries.

It is evident that the effectiveness of washing out pesticide residues depends on several factors: the location of residues, the "age" of residues (as some residues tend to move into deeper layers of commodities with time), the solubility of pesticides and the type of wash. Overall, however, washing of food commodities prior to eating and/or further processing is a highly recommended procedure.
Peeling

Peeling is an important step in the processing of most fruits and vegetables. Whether it is chemical, mechanical, steam or freeze peeling, this method can achieve significant or virtually total removal of pesticide residues from many commodities, depending on their constitution, the chemical nature of the pesticides, and environmental conditions. Peeling has been identified as the most effective procedure for reducing the residues of chlorpyrifos-methyl and fenitrothion in peaches intended for baby food (Balinova et al., 2006).

This preparation method was found very effective in removing chlorfenvinphos, diisopropyl phosphorothioate and monocrotophos from vegetables (Sugibayashi et al., 1996). Most of malathion, lindane, HCB, \( \text{p,p}'-\text{DDT} \) and chlorpropham residues were removed from potatoes by peeling off potato skin (Soliman, 2001; Lentza-Rizos & Balokas, 2001). Peeling also had a significant effect on the removal of chlorpyrifos and its degradation products from potatoes and eggplant (Randhawa et al., 2007). Elimination of lindane, HCB, \( \text{p,p}'-\text{DDT} \) dimethoate, profenofos and pirimiphos-methyl from tomatoes by peeling was at a significantly high level of 80.6-89.2% (Abou-Arab, 1999). The percentages of pesticide residues removed from tomatoes by peeling were 70% for pyridaben and 100% for pyrifluozin and tralomethrin (Boulaid et al., 2005), 77% for procymidone (Cengiz et al., 2007), 62.6-63.9% for chlorpyrifos (Rani et al., 2013), 28% on average for dimethoate, malathion and methyl-parathion, and 100% for chlorpyrifos and ethyl-parathion (Reiler et al., 2015), and over 96% for chlorothalonil, 60% for oxadixyl and over 93% for thiophanate-methyl (Kwon et al., 2015). Chavarri et al. (2004, 2005) reported that 60-73% of chlorpyrifos residues were removed from asparagus by peeling, while they were brought to undetectable levels in peppers. In cucumber, the initial diazinon residue level was reduced by 67.3% by the peeling procedure (Cengiz et al., 2006), while carbaryl was removed up to 40% when cucumber peel was removed (Hassanzadeh et al., 2010).

EFFECTS OF THERMAL TREATMENT ON PESTICIDE RESIDUE DISSIPATION

In the course of various food preparation and preservation processes, food commodities are usually subjected to various thermal treatments, such as drying, pasteurization, sterilization, blanching, steaming, boiling, cooking, frying or roasting, depending on the type of food and aim of processing. Thermal treatments of various food materials may result in the loss of pesticide residues, and the main physicochemical processes responsible for pesticide loss are co-distillation, thermal degradation and/or evaporation, while the chemical nature of specific pesticides dictates which of those will prevail (Sharma et al. 2005). Additionally, if a sample which undergoes heating contains a significant amount of water, it may penetrate the molecules of pesticides and provoke co-distillation along with thermal degradation and evaporation (Cabras et al., 1998).

Drying and dehydration

Drying is a simple traditional method of food preservation. Whether commodities are dried in the sun, oven or a food dryer, the procedure has been found to reduce pesticide residues considerably. Thus, Lee (2001) reported that sun or hot air drying eliminated 20-30% of chlorpyrifos and fenitrothion residues from red pepper, while Mergn et al. (1995) found that industrial dehydration reduced phosalone levels in apples by over 80%. According to Cabras et al. (1998, 1998b, 1998a), sun drying caused greater reductions in pesticide residues than the oven process. Thus, bitertanol decreased by 50% in apricots, dimethoate residues 81% in raisins and iprodion 50% in prunes during sun drying, while oven drying led to 72% dimethoate decline in raisins and even increased bitertanol amount in apricots and phosalone in prunes. Athanasopoulos et al. (2005) also reported 64.2-71.9% loss of methamidophos in grapes dried in the sun, and Shabeer et al. (2015, 2015a) confirmed similar effects for dimetomorph, famoxadone, cymoxanil, pyraclostrobin and metiram residues. The recorded decreases in pesticides were attributed to evaporation of their residues during drying, while the increase in residue levels was most likely due to weight changes during the process.

Pasteurization and sterilization

Pasteurization and sterilization as commercial thermal processing techniques used for food preservation can cause some reduction in residues of various pesticides. Thus, losses of DDT and its metabolites (15.6-58.8%) were reported after milk pasteurization at 65°C for 30 min (Jordral et al., 1995), while residues of diazinon, malathion, chlorpyrifos and \( \text{p,p}'-\text{DDT} \) were reduced by 70.5, 51.9, 44.7 and 29.8% (El-Hoshy, 1997), and lindane by 65-73% (Abou-Arab, 1999a) in pasteurized milk. A somewhat lower effect of pasteurization on
chlorpyrifos reduction (up to 8-10%) in peach puree was reported (Marudov et al., 1999), and there are a few studies reporting lack of pasteurization and sterilization effects on pesticide residue levels (El-Hoshy, 1997; Đorđević et al., 2013a). During industrial processing of tomato, after the pasteurization stage, only insignificant quantities of dimethoate remained, while malathion and parathion were reduced completely (Severini et al., 2003). Sterilization at 121°C for 15 min eliminated maneb residues from tomatoes (Kontou et al., 2004), while milk sterilization caused HCH, DDT and endosulfan reduction of 19, 13 and 11% (Nath et al., 1997) and lindane reduction of 84.4% (Abou-Arab, 1999a). Pirimiphos-methyl reduction was 37.4-49.6% in wheat samples after sterilization (Đorđević et al., 2013), while reduction of chlorpyrifos-methyl in wheat was even more evident after this procedure, reaching 78.8-79.4% (Đorđević & Đurović-Pejčev, 2015).

**Blanching, steaming, boiling, cooking, frying, baking and roasting**

Literature contains reports showing that blanching, steaming, boiling, cooking, frying, baking or roasting have roles in pesticide residues reduction. Cabbage boiling for 30 minutes reduced 80-90% of diazinon and dichlorvos (Kang & Lee, 2005). Potatoes blanching removed 28.3, 22.9, 26.0, 47.3, 46.3 and 45.9% residues of HCB, lindane, p,p'-DDT, dimethoate, pirimiphos-methyl and malathion (Soliman, 2001), while dichlorvos residue concentration in spinach decreased by 72% during blanching for 2 min and 81% during cooking for 20 min (Kang & Lee, 2005). Randhawa et al. (2007) found that the effect of cooking on chlorpyrifos residue reduction was highest on potato, followed by spinach, eggplant and cauliflower (59.6, 48.1%, 28 and 12%, respectively). Cooking of eggplant in boiling water reduced cypermethrin by 41% (Walía et al., 2010), while in cauliflower, cooking reduced the level of quinalphos up to 60% (Lalitha et al., 1998). During boiling for 5 minutes, reductions of α-cypermethrin, azoxyastrobin, bosalid, chlorpyrifos, iprodione, λ-cyhalothrin and pyraclostrobin in broccoli were 34, 81, 69, 43, 87, 34 and 52%, respectively, while the same procedure on tomato reduced azoxystrobin, bosalid, cyprodinil, fluidoxonil and pyraclostrobin by 82, 97, 86, 69, and 75% (Łozowicka & Jankowska, 2016). Cypermethrin residues decreased by 15-33% in cooked and 6-26% in blanched tomato (Kadian et al., 2001), maneb decreased by 74% in tomato cooked for 15 min (Kontou et al., 2004) and no chlorpyrifos residues were detected after tomato cooking, while residue level dropped by 20% after blanching (Chavarri et al., 2005). This correlated with data obtained by Rani et al. (2013), who reported that residues of chlorpyrifos in tomatoes decreased by approximately 28% after boiling. Tomato boiling led also to a reduction in λ-cyhalothrin of up to 20-35% and bifenthrin up to 5-25% (Chauhan et al., 2012; 2012a). El-Nabarawy et al. (1992) and Ismail et al. (1993) reported that home-canning removed most of the organophosphorus pesticides from tomato, and Abou-Arab (1999) revealed that tomato home-canning at 100 °C for 30 min diminished HCB, lindane, p,p'-DDT, dimethoate, profenofos and pirimiphos-methyl residues, and the levels of reduction were 45, 45.4, 30.7, 72.9, 81.6 and 71%. Peppers cooking also reduced the initial amount of chlorpyrifos by 39% (Chavarri et al., 2005), while blanching significantly reduced pyridaben residues (Kim et al., 2015), and there was a 10% reduction of chlorpyrifos in asparagus after blanching and additional 20% after cooking (Chavarri et al., 2005). Considering rice, steaming and/or cooking removed approximately 70% of chlorpyrifos (Lee et al., 1991), and 94.4-100% of dichlorvos, chlorpyrifos-methyl, malathion and fenitrothion (Nakamura et al., 1993), as well as 25% of iprobenfos and 73-100% of fenobucarb (Yang et al., 2012). Malathion was removed from maize grains up to 56.7 and 69.7% by cooking with and without sodium chloride, respectively, and from beans up to 64.2 and 75% by the same treatment (Lalitha & Wandiga, 2002), while blanching led to 100% reduction of procymidone, chlorothalonil and difenoconazole in cowpea (Huan et al., 2015). After cooking in a commercial microwave oven at powers of 500 and 800W for 15-45 min, 92-99% of chlorpyrifos and dichlorvos were eliminated from rice and beans (Castro et al., 2002).

Techniques of frying and baking also proved to be effective for pesticide reduction in vegetables. Thus chlorpyrifos, p,p'-DDT, cypermethrin and chlorothalonil were effectively reduced by up to 86.6, 67.5, 84.7 and 84.8% from cabbage by stir-frying at 100 °C for 5 min (Zhang et al., 2007), microwave- and oven-baking reduced profenofos in potatoes by 98% (Habiba et al., 1992), while potato frying reduced 35.2, 30.1, 35.3, 53.4, 50.5 and 48.7% of HCB, lindane, p,p'-DDT, dimethoate, pirimiphos-methyl and malathion (Soliman, 2001), and 90-98% of thiabendazole, tecnazene and chlorpropham (Lewis et al., 1996). Lalitha et al. (1998) concluded that residues of quinalphos were considerably reduced in eggplant, profenofos was completely removed by blanching and frying for 5 minutes and cypermethrin...
was reduced by 41, 45 and 50% after microwave cooking, frying and grilling, respectively (Radwan et al., 2005; Walia et al., 2010). According to Chavarri et al. (2005), chlorpyrifos was reduced by 67% in peppers during woodfire roasting, and eliminated completely in asparagus and artichoke. Methamidophos, parathion, pirimiphos, chlorpyrifos, ethion and triazophos were reduced by 70.4, 55.4, 38.1, 39.0, 26.3 and 30.5%, respectively, in peppers after 45 minutes of roasting at 100 °C, while malathion and terbuphos were reduced by 16.7 and 40.7% after 60 minutes (Figueiredo et al., 2015). Cowpea frying and stir-frying caused complete reduction of pyridaben, α-cypermethrin, bifentrin, s-fenvalerate and λ-cyhalothrin (Huan et al., 2015).

Considering fruits, the residues of organophosphorous pesticides in strawberries decreased significantly after cooking (Nagayama, 1996), while acetamiprid, boscalid, bupiriminate, chlorpyrifos, cyprodinil, fenhexamid, fludioxonil, folpet, iprodione, pirimicarb, pyraclostrobin, tetraconazole and trifloxystrobin were all highly reduced (34-93%) in strawberries and black currants after boiling for 5 minutes (Łozowicka & Jankowska, 2016; Łozowicka et al., 2016). Apples boiling during home processing significantly reduced residues of fenitrothion (32%) (Rasmusson et al., 2003), while steam boiling (followed by removal of peels/stems) was identified as the most efficient step in terms of a complete elimination of fenitrothion residues from apples during baby food production (Štepán et al., 2005).

Pesticides in foods of animal origin have been found affected by thermal processing as well. Chlorpyrifos residues in eggs decreased by 38% after cooking by scrambling, while all of the pesticide was eliminated by hard boiling in shell (Hsu et al., 1995). Decomposition of HCH, DDT, endosulfan, dimethoate and malathion in cow, goat and chicken meat was affected by cooking and roasting, while cooking was significantly more effective than roasting. The higher degrading ability of cooking over roasting may be attributed to a greater penetration of steam than heat (Sengupta et al., 2010).

**Freezing**

Freezing, as one of the oldest and most widely used food conservation methods, allows preservation of taste, texture, and nutritional value in foods better than any other method. As this process is also based on using extreme temperature, although very low ones, it ranks as thermal treatment. Extremely low temperatures may also be assumed to affect pesticide residues by causing reduction in concentrations. However, there are only a few studies dealing with this issue, and one of them reports that reductions of HCB, p,p'-DDT, lindane, profenofos, pirimiphos-methyl and dimethoate residues in tomatoes were low (4.1-13%) after freezing at -10 °C for three days, and moderate (10.6-32.6%) after freezing for 12 days (Abou-Arab, 1999).

**EFFECTS OF PRODUCT MANUFACTURE ON PESTICIDE RESIDUE DISSIPATION**

Product manufacture is a set of various processing techniques used for converting raw materials into various consumption-ready products. Depending on the employed procedures, techniques and sets of methods - from the simplest grain milling, through oil extraction and processing, juicing/pureeing or canning of fruits and vegetables, to complex bakery and diary production, malting and brewing, wine making and various fermentation processes - the amounts of pesticide residues in final products may differ from those in raw commodities.

**Milling**

As most pesticides used for stored grain protection are contact pesticides, and therefore remaining mostly on the grain surface, milling substantially removes their residues. Thus, wheat grain scouring removed 17-28% more pirimiphos-methyl than conventional cleaning (Brown et al., 1991), and similar results were reported by Sgarbiero et al. (2002) as, compared to whole grain, bran had approximately 2.5 times more pirimiphos-methyl residues, and whole flour had about the same, while white flour had 60% of the residues. Uygun et al. (2005) reported a reduction in malathion residues of approximately 95% in wheat after flour milling.

**Oil extraction**

The amount of various pesticide residues in oil after oil extraction and processing directly depend on hydrophilic/hydrophobic properties of pesticide, whereas various processing stages during the oil refining process could have different effects on pesticide residue elimination. Thus, dichlorvos concentration in soybeans decreased markedly at each stage of the oil refining process, while malathion was reduced at the alkali-refining stage (Miyahara & Saito, 1993). Reduction rates of parathion-methyl, malathion, chlorpyrifos, chlorfenvinphos and dichlorvos, as well as simazine,
endosulfan, oxyfluorfen and diflufenican, were all low after degumming, more or less significant through alkali-refining and bleaching, but at the end all pesticides were removed completely by deodorization at 240-260 °C (Fukazawa et al., 1999; Ruiz-Mendez et al., 2005). Aldicarb, aldicarb sulfoxide, aldicarb sulfone, oxamyl, thiodicarb, carbosulfan and benfuracarb contents decreased by up to 70% by degumming, while these pesticides, as well as methomyl, bendiocarb and furathiocarb, decreased by >80% with bleaching (Fukazawa et al., 2007). Zhao et al. (2014) reported that, when the hot pressing method in soybean oil production was used, it resulted in a significant reduction (92%) of chlorpyrifos after the first step – roasting, but the residue concentration later greatly increased during the pressing process due to retention of the lipophilic pesticide in the oil fraction. When the cold pressing method was used, the residue concentration was overall significantly higher in the final product because of the roasting process responsible for initial reduction was lacking.

**Juicing**

Due to the partitioning properties of the pesticides between the juice and the skin/pulp in fruits and vegetables, residue levels of moderate to highly lipophilic pesticides are expected to be poorly transferred into juices during industrial or domestic juicing processes. A further reduction of residues could be achieved by clarification operations, such as centrifugation or filtering, although, due to the concentration step in juice production, it would not be surprising for pesticide residues to increase. Still, a majority of published results revealed that the technological process of juice production led to pesticide residues reduction in the final products. During the production of concentrated apple juice, more than 90% of fenitrothion residue was removed by pressing and filtration even from unwashed apples (Lipowska et al., 1998), while the production of single-strength apple juice reduced azinphos-methyl, chlorpyrifos, fenvalerate and methomyl by 97.6, 100, 97.8 and 78.1%, and production of apple sauce reduced it all ≥95% (Zabik et al., 2000). In commercial apple juice production, washing, squeezing, sterilization and enzymatic treatment were the key processing steps which caused a final 85-95% reduction of β-cypermethrin, chlorpyrifos, fenvalerate and methomyl by 97.6, 100, 97.8 and 78.1%, and production of apple sauce reduced it all ≥95% (Zabik et al., 2000).

**Bakery production**

Bakery production commonly involves two major steps – fermentation and baking at high temperature, and both could contribute to the degradation of residual pesticides. According to Bolletti et al. (1996), residues of chlorpyrifos-methyl, pirimiphos and malathion were considerably lower in breads than in flours, while bread making caused a significant loss of endosulfan (70%), deltamethrin (63%), malathion (60%), propiconazole (52%), chlorpyrifos (51%) and hexaconazole (46%) in a study by Sharma et al. (2005). Production of bread, spaghetti, Chinese noodles, Japanese noodles, sponge cake and cookies led to chlorpyrifos-methyl and malathion decrease (Hori et al., 1992) and spaghetti processing significantly reduced the concentrations of malathion, fenithrothion, chlorpyrifos-methyl and pirimiphos-methyl (Uygun et al., 2008). The same occurred in cookie processing, as malathion and chlorpyrifos-methyl were significantly reduced by the production technology (Uygun et al., 2009).

**Dairy production**

Various technological processes involved in dairy product manufacture could lead to reductions in pesticide residues in final products. Thus, the initial levels of HCH, lindane and p,p'-DDT in milk were reduced by only 3.5, 3.8 and 2.8% in cheese, but 20.5, 23.3 and 24.6% in butter (Zidan et al., 1994). HCH and DDT residues decreased by 11.54-26.78% and 15.58-35.09% in boiled milk, and 35.86-50.88% and 25.32-62.04% in milk processed by boiling and then fat separation (Madan
highest rates (Sala et al., 1996). Cabras et al. (1995) and settling influenced pesticides to decrease at the and, over the vinification stages, alcoholic fermentation throughout the white and red wine vinification process iprodione and copper oxychloride continuously decreased chlorpyrifos, vinclozolin, chlozolinate, procymidone, with or without maceration (Cabras et al., 2000; Garau et al., 2009). Parathion-methyl, fenitrothion, dichlofluanid, were not determinable in wine at the end of fermentation fenamidone, pyraclostrobin and trifloxystrobin residues usually more evident in red wine than in white wine (Cabras et al., 1991). Therefore the reduction was pesticide reduction than winemaking without maceration wine making with maceration usually leads to greater of pesticides during vinification it was revealed that degradation of malathion, methyl-parathion and exhibited stronger enhancing impact on the degradation lactic acid bacteria at 42 °C for 24h, while malathion was more labile. L. bulgaricus of the same pesticides in skinned milk subjected to simulated yoghurt processing was impacted by microorganisms (Zhao & Wang, 2012). Overall, dimethoate and methyl-parathion were more stable after incubation with L. plantarum gave stronger enhancing impact on the degradation of dimethoate, fenthion and monocrotrophos, while L. plantarum gave stronger enhancing impact on the degradation of malathion, methyl-parathion and trichlorphon.

Vine making

During an extensive research regarding the fate of pesticides during vinification it was revealed that wine making with maceration usually leads to greater pesticide reduction than winemaking without maceration (Cabras et al., 1991). Therefore the reduction was usually more evident in red wine than in white wine production (Stozhoko et al., 2007), although quinoxyfen, fenamidone, pyraclostrobin and trifloxystrobin residues were not determinable in wine at the end of fermentation with or without maceration (Cabras et al., 2000; Garau et al., 2009). Parathion-methyl, fenitrothion, dichlofluanid, chlorpyrifos, vinclozolin, chlozolate, procymidone, iprodione and copper oxychloride continuously decreased throughout the white and red wine vinification process and, over the vinification stages, alcoholic fermentation and settling influenced pesticides to decrease at the highest rates (Sala et al., 1996). Cabras et al. (1995) reported considerable residue reductions of chlorpyrifos-methyl, parathion methyl and quinalphos (>80%) and moderate reduction (ca. 50%) of methidathion during vinification after 15 days, while, additionally, the clarifying agent charcoal led to complete or almost complete elimination of insecticide residues. Fluazinam and mepanipyrim were highly impacted by fermentation during wine making, and tetraconazole was removed mainly during must clarification, thus residues of those fungicides were negligible in the final product (Cabras et al., 1998c). Soleas & Goldberg (2000) reported that clarifying agents proved to have a significant role in pesticide removing during vinification. Will et al. (1999) showed that must clarification, fermentation and racking were all important steps in reduction of pesticides, and the reduction occurred due to hydrolysis and absorption on suspended matter. Red wine malolactic fermentation using Oenococcus oeni resulted in significant reductions in chlorpyrifos, dicofol, chlorothalonil and procymidone concentrations, up to 70, 40, 35 and 25%, respectively (Ruediger et al., 2005), while alcoholic fermentation (with Saccharomyces cerevisiae) and malolactic fermentation (with O. oeni) eliminated tebuconazole by 86% in the final red wine product (González-Rodríguez et al., 2009).

Malting and brewing

During malting and brewing, fermentation is the main production stage but only one that is responsible for the overall pesticide reduction in final products. Pesticide residues present in grain and hops dissipate throughout the beer production process (Farris et al., 1992). During malting, it was revealed that fenithrothion, phenthoate and triflumizole were considerably reduced through steeping and kilning (Miyake et al., 2002). Soleas & Goldberg (2000) reported considerable residue reductions of chlorpyrifos-methyl, fenamidone, pyraclostrobin and trifloxystrobin residues were not determinable in wine at the end of fermentation with or without maceration (Cabras et al., 2000; Garau et al., 2009). Parathion-methyl, fenitrothion, dichlofluanid, chlorpyrifos, vinclozolin, chlozolate, procymidone, iprodione and copper oxychloride continuously decreased throughout the white and red wine vinification process and, over the vinification stages, alcoholic fermentation and settling influenced pesticides to decrease at the highest rates (Sala et al., 1996). Cabras et al. (1995) reported considerable residue reductions of chlorpyrifos-methyl, parathion methyl and quinalphos (>80%) and moderate reduction (ca. 50%) of methidathion during vinification after 15 days, while, additionally, the clarifying agent charcoal led to complete or almost complete elimination of insecticide residues. Fluazinam and mepanipyrim were highly impacted by fermentation during wine making, and tetraconazole was removed mostly during must clarification, thus residues of those fungicides were negligible in the final product (Cabras et al., 1998c). Soleas & Goldberg (2000) reported that clarifying agents proved to have a significant role in pesticide removing during vinification. Will et al. (1999) showed that must clarification, fermentation and racking were all important steps in reduction of pesticides, and the reduction occurred due to hydrolysis and absorption on suspended matter. Red wine malolactic fermentation using Oenococcus oeni resulted in significant reductions in chlorpyrifos, dicofol, chlorothalonil and procymidone concentrations, up to 70, 40, 35 and 25%, respectively (Ruediger et al., 2005), while alcoholic fermentation (with Saccharomyces cerevisiae) and malolactic fermentation (with O. oeni) eliminated tebuconazole by 86% in the final red wine product (González-Rodríguez et al., 2009).

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very low amounts (Hengel & Shibamoto, 2002). Malting, milling, boiling and cooling steps during the brewing process did not affect triadimefon residues significantly but fermentation highly promoted its degradation (Kong et al., 2016).

**Fermentation**

Fermentation as one of the oldest simple biotechnological processes is implemented in the production of various other foods besides pastry, dairy, wine and beer, and reduction in pesticide residues during fermentation has been recorded in the majority of those commodities. Thus, fermentation in meat products (fermented sausage) reduced DDT and lindane residues by 10 and 18%, and these reductions were due to the activity of meat starters *Lactobacillus plantarum* and *Micrococcus varians* (Abou-Arab, 2002). Miyahara and Saito (1994) reported that dichlorvos was easily removed in every stage of tofu production. During kimchi fermentation, chlorpyrifos was degraded rapidly (83.3%) and the chlorpyrifos-degrading lactic acid bacteria were identified as *Leuconostoc mesenteroides*, *Lactobacillus brevis*, *Lactobacillus plantarum*, and *Lactobacillus sakei* (Cho et al., 2009), while organophosphorus hydrolase was shown to be responsible for pesticide degradation during this fermentation process (Islam et al., 2010). Jung et al. (2009) reported that bifenthrin and metalaxyl were also effectively removed during kimchi fermentation, up to 57.8-72.2% and 81.0-85.6%, respectively. Fermentation with *Lactobacillus plantarum* showed to be an effective tool for reduction of pirimiphos-methyl (15-34%) and reduction of bifenthrin (16-42%) from wheat (Đorđević et al. 2013; 2013a; Đorđević & Đurović-Pejčev, 2016). Concentration of chlorpyrifos-methyl was significantly reduced (14.8-19.0%) as a result of wheat fermentation by the yeast *Saccharomyces cerevisiae* (Đorđević & Đurović-Pejčev, 2015). Finally, the same yeast was proven to be effective for moderate reduction of bifenthrin residues from wheat (maximum 17%) (Đorđević & Đurović-Pejčev, 2016). Regarding pesticide residue loss during fermentation, there are several possible scenarios. Some researchers presume that there is a high possibility that pesticide dissipation influenced by microorganisms is a consequence of pesticide adsorption on the polysaccharides in the cell walls. However, others believe that once microbes get into the surroundings contaminated with pesticides, they will utilize those chemicals as a nutrition source in order to provide a sufficient amount of carbon, nitrogen and phosphorus required for cell growth, or they will simply, striving for environmental decontamination, produce pesticide degrading enzymes responsible for biological degradation.

**Infusion**

During preparation of tea and coffee, the two most popular beverages throughout the world, both the tea leaves and coffee beans processing and the infusion process could reduce pesticide residues. Jaggi et al. (2000) found that a major amount of quinalphos (64%) was lost during tea processing, and only 16% of the pesticide was transferred into cup-infusion. Acetamiprid and imidacloprid residues during black tea manufacture decreased 20-22% during withering, rolling and fermentation, and additional 10-15% during drying, whereby the final percentage of transfer during tea infusion was approx. 45-48% for acetamiprid and 37-39% for imidacloprid (Gupta & Shanker, 2009). Transfer of propargite residues from tea to infusion was 23.6-40.0% (Kumar et al., 2005), while bifenthrin transfer was even lower, 1.5-14% (Tewary et al., 2005). Similarly, coffee beverage preparation decreased the levels of dichlorvos and methyl-parathion by 55-74 and 82-88%, respectively (Oliviera et al., 2002).

**CONCLUSION**

The levels of pesticide residues that remain in food commodities as a result of pre- and postharvest treatments could be effectively decreased by various food preparation steps and processing into different products. Thus, common, simple and cost-effective processing techniques may lead to remarkable reductions in the content of harmful pesticides in final food products. The extent of reduction varies with the nature of pesticides, type of commodity and processing steps. As pest management is and will remain one of major inputs in agricultural production, this topic needs great attention in order to provide safe foods, while at the same time maintaining cost-effective production and aiming to avoid medical expenses for treatment of resulting ailments.

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Prerada hrane kao sredstvo za smanjenje ostataka pesticida

REZIME

Zadovoljavajući prinosi u današnjoj savremenoj poljoprivredi gotovo su u potpunosti zavisni od upotrebe pesticida. Međutim, neadekvatna primena ovih agrohemikalija može dovesti do akumuliranja veće količine ostataka u životnoj sredini, što za posledicu ima i povećanje zagađenosti uzgajanih konzumnih biljaka. Porast kontaminacije prehrambenih proizvoda pesticidima sa ozbiljnim posledicama na ljudsko zdravlje doveo je do povećane zainteresovanosti za razvijanje jednostavnih i isplavljive strategije u cilju poboljšanja bezbednosti hrane sa aspekta zagađenosti ovim jedinjenjima. Utvrđeno je da brojne tehnike procesuiranja hrane, kako na industrijskom nivou tako i u domačinstvima, mogu da dovedu do smanjenje nivoa zagađenosti pesticidima, pri čemu stepen smanjenja ostataka pesticida zavisi od hemijskih karakteristika pesticida, vrste prehrambene sirovine i načina procesuiranja hrane. Tako kontaktni pesticidi i ograničeni sistemici mogu da se uklone u značajnoj meri jednostavnom pranjem prehrambene sirovine vodom ili različitim hemijskim rastvorima, pri čemu stepen smanjenja ostataka prisutnog pesticida zavisi od njegove rastvorljivosti u vodi i/ili korišćenom rastvoru. Takođe, u zavisnosti od hemijske prirode pesticida i vrste prehrambene sirovine, ljutenje voća i povrća može dovesti do uklanjanja ostataka pesticida na zadovoljavajućem nivou. Različite tehnike termičke obrade hrane (sušenje, pasterizacija, sterilizacija, blanširanje, barenje, kuhanje, prženje, pečenje), koje se koriste u procesu pripreme i konzervisanja prehrambenih proizvoda, mogu da dovedu do smanjenja ostataka pesticida putem isparavanja, kodestilacije i/ili termalne degradacije. Osim toga, procesi proizvodnje hrane, od najjednostavnijeg mlevenja žita, preko proizvodnje ulja, sokova, kaša, konzerviranog voća i povrća, do složenih procesa proizvodnje piva, vina, pekarskih, mlečnih i brojnih drugih fermentisanih proizvoda, imaju značajnu ulogu u smanjenju zagađenosti pesticidima. U ovom radu dat je prikaz brojnih različitih primera uticaja tehnika procesuiranja hrane na smanjenje ostataka pesticida u finalnim proizvodima.

Ključne reči: Pesticidi; Ostaci; Prerada hrane