

# Fate of Pesticide Residues on Raw Agricultural Crops after Postharvest Storage and Food Processing to Edible Portions

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## 1. Introduction

Most analyses of pesticide residues in foods are being performed in Raw Agricultural Commodities (RAC) for a variety of purposes, which include regulatory monitoring, import/export certification, risk assessment, field-application trials, organic food verification, and marketing to consumers. The levels of the positive detections in these analyses are generally being estimated on the basis of established Maximum Residue Limits (MRL's) which are set using field trial data for a particular pesticide to arrive at the highest residue levels expected under use according to Good Agricultural Practice (GAP). MRL's are a credible and useful means of enforcing acceptable pesticide use, and satisfy most of the above mentioned purposes of monitoring pesticide residues in the different food of plant origin. However, MRL's use, proved to be inadequate as a guide to pesticide residue consumption through nutrition in health risk assessment studies from residues in food of plant origin and this is mainly because a wide range of RAC's are processed before they are consumed.

Storage and other post-harvest practices prior the further management of the product, as well as household and industrial food preparation processes may alter pesticide residues as compared with raw crops via chemical and biochemical reactions (hydrolysis, oxidation, microbial degradation etc.) and physicochemical processes (volatilization, absorption etc.). Although these processes usually are leading to reduction of any residues left on crops at harvest (Kaushik et al. 2009; Holland et al., 1994), in special cases residues may concentrate in the final product (e.g in the production of dry fruits and unrefined vegetable oil) (Amvrazi & Albanis 2008; Guardia Ruibio et al., 2006; Lentza-Rizos & Avramides, 2006; Lentza-Rizos & Kokkinaki, 2002; Cabras et al., 2000; Cabras et al., 1998; Cabras et al., 1997a; Holland et al., 1994; Cabras et al., 1993; Leandri et al., 1993; Ferriera & Tainha, 1983) and/or be formed in more toxic by-products or metabolites of the pesticide parent compound on raw crop (Holland et al., 1994; WHO 1988). These considerations suggest that effects of post-harvest practices and food processing should be taken into account on the fate of a pesticide residue during dietary exposure assessments so as to ensure consumer safety from pesticide residues and allow a more realistic calculation of the dietary burden of livestock.

Food processing studies and their effects on pesticide residues are also very important for the monitoring of the cases that the final residue concentration is exceeding MRL in RAC.

Although the established MRLs for processed and ready to eat food are limited to present and concern mainly the processed commodities where the residue could be found concentrated, regulatory attention has been focused on this issue the last decade and a current confrontation practice is the perspective of the processing factors ( $P_f$ 's) establishment to be used with already specified MRL's of pesticides in RAC's (Codex Alimentarius Commission, 2007).  $P_f$  is defined as the ratio of the residue level in processed commodity to the residue level in RAC or in the commodity to be processed.

The aim of this chapter is to review the main types of post-harvest and processing practices that typically RAC's are being subjected prior their consumption and point out the effects that these processes cause on the fate of pesticide residues that may persist on and in RAC's after harvest. The main chemical, biochemical and physical phenomena in which pesticide residues take part in during these processes and the parameters that may influence these phenomena would further be discussed, through the latest published data on this topic.

## 2. Mechanisms and factors affecting the fate of pesticide residues during storage and food processing

The most important mechanisms that may lead in of a possible residue alteration during storage and other household and industrial food preparation processes of RAC are summarized as follows:

1. *Dissolution*. The dissolution of a pesticide residue may take place during the washing of RAC, grape vinification, tea preparation and boiling and theoretically is related with the water solubility of the pesticide residue. Other factors such as the type of formulation applied, temperature, initial concentration of the pesticide residue on RAC, pesticide Kow, ionic strength and pH of the aqueous media and the nature of RAC may further affect the pesticide dissolution mechanism in a certain food preparation process.
2. *Heat degradation*. Frequently a number of pesticides undergo degradation, polymerization and other reactions by heating. The reactions proceed at a greater rate in the liquid phase rather than in solid state. Thermal unstable compounds (e.g. atrazine, alachlor, aldicarb, captan, daminozide, dimethoate, dodine, lenacil, phorate, and others) may significant reduced by the formation of their degraded products during cooking and oven-drying of the processed RAC. Heat may also affect almost all pesticide eliminating mechanisms occur during RAC processing (dissolution, hydrolysis, penetration, volatilization, microbial degradation, metabolism and enzymatic transformation).
3. *Hydrolysis*. Hydrolysis is one of the basic processes of most pesticides elimination through the different storage and food preparation processes of RAC. Most pesticide residues may be hydrolyzed during typical RAC processing depending on the water added or the moisture on RAC, pH, temperature and pesticide's concentration. Pesticide compounds with functionalities such as carbamate, amide, urea, thiocarbonyl and imino group are more readily hydrolyzed in the presence of trace amounts of acid and/or base during the different processes of food preparation.
4. *Metabolism (enzymatic transformation); Microbial degradation*. The enzymatic transformation of pesticides is mainly the result of biotic processes mediated by plants and microorganisms. Penetrated pesticides may be further metabolized during the storage of fresh fruits and vegetables. Microbial degradation is the breakdown of pesticides by microorganisms. It occurs when fungi, bacteria, and other microorganisms consume pesticides along with other substances. Microbial degradation is usually

mediated by enzymes. Microbial activity usually is greatest at 10-45°C and is enhanced by moisture, air and neutral pH. Thus pesticides microbial degradation may take place during the processes where these conditions exist as it happens in grain storage. Other processes of RAC where the metabolism of pesticides may occur are those include a fermentation step (bread making, alcoholic beverage production, vinegar production etc).

5. *Oxidation.* Organic pesticide residues on RAC could be oxidized rather slowly with oxygen or air during storage depending on the of the pesticide residue and on the nature of RAC. In general the degradation of pesticides through chemical oxidation is affected by all factors that may result in the formation of .OH radicals. Food exposure to air, high storage temperatures, UV irradiation, and the presence of pro-oxidant compounds in the media where the pesticide residue occurs are several factors that may enhance the oxidation process of the persistent pesticide residue. In conclusion pesticides chemical oxidation mechanism may takes place during long term storage at elevated temperatures (i.e. room temperature), during the washing of RAC with oxidizing agents such as the ozone and H<sub>2</sub>O<sub>2</sub> (or combination) and or UV irradiation of the ready to eat food for preservation purposes.
6. *Penetration.* Penetration is the most common physicochemical process that may take place on the surface of RACs from the time of the pesticide application to the end of the storage of RAC. The degree of a pesticide residue penetration on a RAC significantly affects its fate during RAC storage, washing, peeling, and drying. The main factors that may affect the penetration of a pesticide residue are the characteristics of the pesticide (Kow, the molecular weight, the probable systemic action, and the formulation of applied pesticide) in relation with the nature of RAC. The initial concentration of the pesticide residue on RAC and the processing temperature could also affect significant the penetration mechanism.
7. *Photodegradation.* All pesticides are susceptible to photodegradation to some degree. The intensity and spectrum of sunlight, length of exposure, and properties of the pesticide affect the rate of pesticides photodegradation. After harvest, photodegradation is not suspended to take place on pesticide residues persist on RAC in common food preparation processes and food storage. However significant pesticide elimination through photo degradation may occur during food processing like sun drying of fruits and UV irradiation that may be used for post harvest preservation processes.
8. *Physical change of the concentration of the pesticide residue due to a possible change of the RAC's weight.* Typical examples of that type of changes are: (i) the RAC's growth (namely plant growth) during the storage of immature fresh fruits that usually lead to lower concentration in the stored RAC, and (ii) the loss of water during the storage, cooking and/or drying of RAC that usually leads in higher concentrations of the pesticide residue in the stored or processed RAC. A phase separation from RAC in food processing may also lead in a physical change of the pesticide residue depending on the partition coefficient of the pesticide in the edible part of RAC and the mass of the separated phase in the final product. A typical example of these types of changes is the concentration of fat soluble pesticides and the respective elimination of water soluble pesticides in unrefined oil production.
9. *Volatilization and co-distillation.* Non systemic pesticide residues on RAC with relative high vapour pressures and low Kow may significant be eliminated through

volatilization from the stored or prepared food after drying or cooking. During storage, the higher the temperature is, the higher the pesticide's volatilization from the surface of the RAC and the greater the air humidity is, the less pesticide volatilizes whereas the nature of the RAC (e.g. water content, % w/w) may also play a significant role on these processes of pesticides elimination from RAC.

### 3. Fate of pesticide residues during post harvest storage practices of RACs

Proper storage of unprocessed food of plant origin includes maintaining at appropriate temperatures, away from light, under the proper percentage of humidity and in such a way to keep it clean and safe prior the further management of the product. Temperature control is the single most important factor in maintaining quality after harvest and the most common postharvest practice of plant commodities storage is cold storage.

Cold storage is taking place at different temperature and humidity, and lasts for different time intervals for each RAC depending from the nature of the commodity. Keeping products at their lowest safe temperature (0-4 °C for temperate crops, 4-8 °C and above 8 °C for chilling sensitive crops) will increase storage life by lowering respiration rate, decreasing sensitivity to ethylene gas and reducing water loss. However, temperature may additionally control the following elements of a pesticide residue dissipation and/or alterations during storage: (a) pesticide volatilization, (b) pesticide penetration, (c) pesticide metabolism and/or enzymatic degradation through the control of crop respiration and the consequent control of crop metabolism, (d) pesticide degradation through the retarding of certain microbial growth rate and activity, and (e) pesticide concentration changes per kg of RAC due the reduction of moisture loss, and/or loss of dry weight from respiration, or due to crop growth that usually leads to a reduction of pesticide concentration on raw crop. Furthermore, photodegradation is not expected to reduce further the applied pesticide after harvest during the proper storage of raw crop away from light whereas hydrolysis does not occur readily on plant surfaces during storage and is primarily confined to absorbed materials. In consequence, pesticide residues during deep frozen storage (-10 to -20 °C) are expected to be stable or decay rather slowly. However, the higher the storage temperature and time of storage, the higher the pesticides dissipation, degradation or concentration in processed commodity will be whereas the initial pesticide concentration and its physicochemical properties may affect significant its stability through storage processes.

*Residues on Fruits and Vegetables.* Results of studies performed with fortified fresh fruits and vegetables with different pesticides in order to study the main effects on pesticide residues during storage indicated that the main mechanisms of pesticide residues reduction through storage are the volatilization and the slow acidic hydrolysis (since most fresh fruits have a pH=3-4). Both processes are being controlled significantly by the penetration mechanism.

Thus, although many pesticides studied (azinphos methyl, kresoxim methyl, tolylfluanid, methamidophos, fenthion) in cold storage of different RAC (apples, lemons, grapes) exhibited slow dissipation rates ( $t_{1/2}$ : 42-267days), or found to be stable during storage (pyrethroids and carboximides in apples) (Athanasopoulos et al., 2005; Kyriakidis et al., 2005; Athanasopoulos et al., 2003; Rasmussen et al., 2003; Athanasopoulos & Pappas, 2000), the highly volatiles dichlorvos and diazinon dissipated rapidly (70.8% and 64.8% respectively) from cucumber stored at +4 °C for 6 days (Cengiz et al., 2006) and the same results have been reported for dichlorvos from asparagus and kiwifruit stored at +1 °C for (Holland 1994).

Rasmussen et al. (2003) reported that the organophosphates chlorpyrifos, diazinon and fenitrothion were significantly reduced (from 25% for chlorpyrifos to 49% for fenitrothion) on apples during storage at 4 °C for 79 days, whereas quinalphos was not. Quinalphos exhibits a systemic effect and penetrates from the skin into the outer flesh of the fruits such retarding dissipation during storage through the processes taking place on fruit surface. The same low dissipation through storage (~19% and 38% reduction on tomatoes after storage at +4 °C for 7 and 14 days respectively in polyethylene bags) could be observed for procymidone (Cengiz et al., 2007) that exhibits also a systemic action as compared with other pesticide dissipation with no systemic action during tomatoes storage (54 and 64% reduction for captan in the same study and > 49% reduction of iprodione and thiacloprid in another study performed by Omirou et al. 2009 at different storage conditions; +15 °C for 7 and 12 days). However, the reduction of pirimicarb (52.7%), cyprodinil (33.83%), tebuconazole (19.34%) with systemic action as compared with the non systemic insecticides fludioxonil (28.8%), pyriproxyfen (8.26%, not significant) and buprofezin (2.55%, not significant) did not present similar differences on their reduction during cold storage of peppers (Fenoll et al., 2009) suggesting that octanol/water partition coefficients were also well correlated with penetration mechanism of pesticides in peppers (Kow: pirimicarb < tebuconazole ~ cyprodinil < fludioxonil < buprofezin < pyriproxyfen). Furthermore, it should be noted that pirimicarb and cyprodinil are unstable in basic pH as is pH of peppers (>5). Similar effects of the commodity pH on pesticides dissipation during storage have been reported by Athanasopoulos & Pappas (2000) when studied dissipation rates of azinphos methyl in apples and lemons at their typical storage conditions and a significant lower dissipation rate was observed for azinphos methyl on lemons than in apples. The differences were attributed, to the differences in acidity among the two commodities studied. The differences on the reduction of pesticides during storage of different RACs are also very pronounced in current literature and except of the observed different dissipation rates among the different commodities, significant differences were observed and among the different varieties of the same commodity studied (Rasmussen et al., 2003).

*Grain storage.* A separate, big issue on the fate of pesticide residues on RAC during storage concerns the pesticide residues on grains. Although grains storage is being performed at ambient temperature, in bulk silos for long term (3 - 36 months), the dissipation of pesticides is a slow process as compared with the cold storage of fruits and vegetables mainly due to pesticide retention on the seed coat and/or the high degree of pesticides penetration from the seed coat to the bran and germ which contain high levels of triglycerides. Furthermore, during grain storage insecticides may be applied post-harvest to reduce losses from storage pests (Holland, 1994), thus making cereal grains a potent source of pesticide residues through diet exposure.

The most widely studied insecticides in grain storage are the organophosphates malathion, pirimiphos methyl, chlorpyrifos methyl and their dissipation after 5-8 months of storage could ranged from 50-86% depending of pesticide Kow, type of applied formulation and storage temperature and humidity ( Uygun et al., 2009; Uygun et al., 2008; Uygun et al., 2007; Balinova, 2006; Uygun et al., 2005). The mechanism proposed was that insecticides adsorbed to the grain are desorbed by water and become available for degradation by storage fungi, enzymes, metal ions and other active molecules (Holland 1994). Different classes of insecticides have also been studied and their dissipation during grain storage was found higher for natural pyrethrin residues (a complete disappearance was observed by Caboni et al. 2007 after 8 months of storage at ambient temperature) and lower for organochlorines and synthetic pyrethroids that are very stable under the reported main

mechanisms of dissipation through typical storage conditions (non volatiles, with high  $K_{ow}$  values and stable in hydrolytic processes).

#### **4. Fate of pesticide residues during common domestic and industrial processing of RACs**

The processing of food commodities generally implies the transformation of the perishable raw commodity to a value added product that has greater shelf life and is closer to being table ready. In this section the fate of pesticide residues during the most common food processing techniques applied to RAC in both household and industrial processing (washing; removal of the outer parts of the RAC such as peeling, husking, hulling, shelling, and trimming; comminution such as blending, chopping and mincing; cooking, and juicing) and the most important industrial processing of RAC in terms of frequent consumption of the processed food and/or the high probability of pesticide residues concentration in the processed ready to eat food (grain milling, oil production, alcoholic beverages production and drying), are being described.

##### **4.1 Washing**

Washing of RAC is the preliminary step in both household and commercial food preparation and the effect of washing on the fate of the pesticide residues on RAC has been well studied and recently well reviewed (Kaushic & Naik, 2009; Zabik et al., 2000; Krol et al., 2000; Holland, 1994). The most interesting conclusions of these studies are that the rinsability of a pesticide is not always correlated with its water solubility (Cengiz et al., 2007; Boulaid et al., 2005; Angioni et al., 2004; Krol et al., 2000) and that different pesticides may be rinsed from processed units of RAC by different washing procedures (Angioni et al., 2004; Pugliese et al., 2004; Lentza-Rizos & Kokkinaki, 2002; Cabras et al., 1998b).

The removal of pesticides with the washing of RAC may be performed not only through the dissolution of pesticide residues in the washing water or the rinsing with chemical baths (detergents, alkaline, acid, hypochlorite, metabisulfite salt, ozonated water etc) (Holland, 1994) but also through the removal of dust or soil particles previously absorbed residues from the outer layer of RAC (Guardia Rubio et al., 2007; Guardia Rubio et al., 2006; Angioni et al., 2004; Cabras et al., 1997). Penetration is again the most dynamic process that may control the fate of a pesticide residue on RAC during washing. The systemic insecticide dimethoate with water solubility equal to 23300mg/L and quinalphos that exhibits systemic action and its water solubility is 18 mg/L, were not reduced during the washing of olives (Cabras et al., 1997). Furthermore in many studies washing was not related with the water solubility of the pesticide residue but with  $K_{ow}$  such reinforcing the view that partition coefficients between cuticle and washing water correlate well with pesticides  $K_{ow}$  (Baur et al., 1997). In consequence, the use of an appropriate detergent that has the ability to solubilise waxes may dissipate the residue present in the fruit's epicuticular wax layer (Angioni et al., 2004). Other washing agents or dipping treatments may also lead in the selective removal of the pesticide residues with systemic action through similar mechanisms (Cabras et al., 1998b; Femenia et al., 1998). The residue still present in the fruit after washing can be ascribed to the pesticide that has penetrated into the cuticle. The formation of possible toxic by-products during washing has also been studied by several authors (Ou-Yang et al., 2004; Pugliese et al., 2004; Cabrera et al., 2000; Zhang & Pehkonen, 1999). According to these results, typical washing with tap water is not expected to form toxic metabolites whereas the use of high levels of sodium hypochlorite, hydrogen peroxide, and

potassium permanganate in washing water as well as ozonated water could form oxons from the organophosphorus pesticides by chemical oxidation (Ou-Yang *et al.*, 2004; Pugliese *et al.*, 2004; Cabrera *et al.*, 2000; Zhang & Pehkonen, 1999).

#### **4.2 Peeling (husking, hulling, shelling, trimming)**

The removal of the outer part of RAC by peeling, husking, hulling, shelling, or trimming is the most effective food preparation process for pesticide residues removal from RAC. Numerous studies report the elimination of different pesticide residues on different RAC through peeling to range from 70 to 100% (Cengiz *et al.*, 2007; Boulaid *et al.*, 2005; Fernández-Cruz *et al.*, 2004; Rasmussen *et al.*, 2003; Burchat *et al.*, 1998; Clavijo *et al.*, 1996; Celik *et al.*, 1995; Holland, 1994; Rouchaud *et al.*, 1991).

The systemic action of a pesticide residue in this case is not always correlated with decreased reduction of pesticide residues through peeling. Thus, although, residues of the systemic organophosphorus phorate were only reduced by 50% through peeling of potatoes (JMPR, 1992) and similarly disyston residues in potatoes were only reduced by 35% after peeling (Holland 1994), quinalphos residues on apples and procymidone residues on tomatoes were reduced by  $\geq 73\%$  (Cengiz *et al.*, 2007). Furthermore, the reported data of the reduction of dichlorvos and diazinon on cucumber by 57.2% and 67.3% respectively (Cengiz *et al.*, 2006), the low reduction of pyridaben (~70%) in tomatoes (Boulaid *et al.*, 2005) and the lower reduction of the metabolites of fenitrothion (80-92% for fenitrothion, 78-99% for fenitrothion oxon and 73-78% for 3-methyl-4-nitrophenol) in kakis (Fernández-Cruz *et al.*, 2004) and endosulfan sulphate (24%) in apples (Rasmussen *et al.*, 2003) consist that the main factor that may affect negatively that satisfactory removal of pesticide residues from RAC is penetration into the flesh of the processed RAC that is controlled by the physicochemical properties of the pesticide residue in relation with the nature of the processed agricultural commodity.

#### **4.3 Comminution**

Comminution of RAC through chopping, blending, crushing and similar processes usually do not affect pesticide residues in RAC since most pesticides are relatively stable in acidic plant tissue homogenates for the moderate periods of time involved in food preparation. However, comminution leads to release of enzymes and acids which may increase the rate of hydrolytic and other degradative processes on residues that were previously isolated by cuticular layers. Special concern on the fate of residues should be paid on acid sensitive pesticide compounds (e.g. EBDC, carbosulfan, benfuracarb, pymetrozine, dioxacarb, thiodicarb and others) that readily are hydrolyzed in the presence of trace amounts of acids and the most toxic metabolites formed should be studied. A typical example is the rapid degradation of ethylene bis dithiocarbamate (EBDC) fungicide residues to the formation of the toxic ETU, carbon disulphide and ethylenediamine in slightly acidic media, similar to the pH of the tomato homogenates (4.0-4.2) (Kontou *et al.*, 2004; Holland, 1994; Howard & Yip, 1971). Pesticides degradation processes during storage of blended RACs could be enhanced significant with the increase of time storage and temperature and more toxic metabolites in these cases should be taken into consideration in health risk assessments.

#### **4.4 Juicing**

The residue levels in juices from fruits or vegetables are generally reduced by 70-100% (Rasmussen *et al.*, 2003; Zabik *et al.*, 2000; Abou-Arab, 1999; Will & Krüger, 1999; Buchat *et*

al., 1998; Holland, 1994) and their reduction depends on the partitioning properties of the pesticide between the fruit skin, pulp and the juice (which generally contain some solids). The pulp or pomace by-products, which often include the skin, retain a substantial proportion of lipophilic residues.

Rasmussen et al. (2003) reported that only 2-9% of different pesticide residues (chlorpyrifos, cypermethrin, deltamethrin, endosulfan, fenitrothion, fenpropathrin, iprodione, kresoxim-methyl,  $\lambda$ -cyhalothrin, vinclozoline) on fortified apples were transferred in apple juice whereas in apple pulp residues in mg/kg were detected 2.0-3.5 higher than in unprocessed apples (due to mass concentration). In the same study quinalphos (systemic action), endosulfan sulphate and tolylfluanid that were detected in higher amounts in the flesh of apples were transferred also in higher amounts in the produced apple juice ( $\leq$ 19%, 13% and 23% respectively). No correlation with the water solubility of the pesticides studied could be observed on their fate during juicing in results reported by Abou-Arab (1999) where the reduction of HCB, lindane, p,p-DDT, dimethoate, profenofos and pirimiphos-methyl, residues upon tomato juicing, ranged from 72.7% to 77.6%. However, in other studies pesticides with the highest water solubility were present in relatively higher amounts in the juiced carrots, tomatoes and strawberries (Will & Krüger, 1999; Buchat et al., 1998).

Clarification by filtration or centrifugation in juice processing may further eliminate pesticide residues retained in suspended particles (Liapis et al., 1995; Miliadis et al., 1995) and juice concentration by vacuum may also concentrate the pesticides transferred in juice (Zabik et al., 2000).

#### **4.5 Cooking (cooking, boiling, frying)**

Pesticide residues might be vaporized, hydrolysed and/or thermal degraded during cooking. However, the processes and conditions used in food cooking are highly varied. The details of time, temperature, degree of moisture loss, whether the system is open or closed and whether water is added or not in the process are important for the estimation of the fate of a residue level. In general, rates of degradation and volatilization of residues are increased by the heat involved in cooking or pasteurization and rates of hydrolysis may also be increased by the water addition and the increase of temperature.

In different studies of organophosphorus (OP) insecticides (fenitrothion, fenitrothion oxon, 3-methyl-4-nitrophenol) on RACs (cauliflower, kaki fruits ) it was reported that OPs are stable through heating without the addition of water for 10-15 min (Fernández-Cruz et al., 2006; Fernández-Cruz et al., 2004) and unstable to heating in aqueous solution. Coulibaly & Smith (1993) studied famphur, fenthion, parathion, stirofos, chlorpyrifos, and ronnel in aqueous solutions that were unheated, heated to 70 °C for 1 or 2 h, and heated to 80 °C for 1 h. Stirofos and famphur were largely unaffected by heating whereas fenthion, parathion, chlorpyrifos and ronnel were hydrolyzed by 53.2%-80% in unheated water and further heating did not result in further degradation. Other studies confirm the reduction of OPs (32% reduction of fenitrothion and 89.5% reduction of triazophos) after boiling (Rasmussen et al., 2003 ; Holden et al., 2001), but also reported chlorpyrifos and acephate reduction (50.5-68%) after cooking of peppers, asparagus and peaches without the addition of water (at 100-110°C for 20-80 min) (Chavarri et al., 2005). The latter differences might be due to higher temperatures and times used in cooking processes since drying at elevated temperatures and/or times also lead in higher reduction of pesticides (including OPs) in processed commodities. Furthermore, Nagayama (1996) reported that during the cooking process, some residual pesticides were translocated into the cooking water from the raw materials



according to the water solubility expression, and the pesticide remained in the processed food according to the Kow expression. These relationships were shown by simple equations. The inclination of the regression expression was similar with the same cooking process and increased with cooking time.

Other pesticides such as pyrifenoxy, pyridaben, and tralomethrin were not reduced after cooking applied to the tomatoes without the addition of water although residues were concentrated in the final product due to water loss through cooking by a factor of 1.9-3.0 (Boulaid et al., 2005). Captan was almost completely eliminated after cooking cauliflower without water for 15 min and after the processing of apple to sterilized puree (125 °C for 20 min at pH 4) by exhibiting its tendency to thermal degradation.

Interestingly, boiling did not reduce chlorpyrifos, cypermethrin, deltamethrin, diazinon, endosulfan (alpha, beta and endosulfan sulphate), fenpropathrin, iprodione, kresoxim methyl,  $\lambda$ -cyhalothrin, quinalphos and vinclozoline residues on apples (Rasmussen et al., 2003). The fact that in the same study fenitrothion and tolylfluanid were reduced by boiling was not attributed to the acid hydrolysis of pesticides but to the selective degradation of fenitrothion and tolylfluanid residues related to interaction with thiol-containing compounds present in apples. Fenitrothion was the only organophosphorus pesticide in that study that contained a methoxy group enhancing enzymatic degradation to ethoxy containing organophosphorus pesticides whereas the possible proposed degradation of tolylfluanid was the cleavage of the N-S bound after tolylfluanid interaction with thiol compounds.

Randhawa et al. (2007) studied the fate of chlorpyrifos and its degradation product 3,5,6-trichloro-2-pyridinol during boiling of different vegetables with water and the decrease of chlorpyrifos ranged from 12% to 48%. The effect was more obvious in spinach (38%) followed by cauliflower (29%). 3,5,6-trichloro-2-pyridinol was substantially increased during the course of cooking consisting that metabolites of toxicological concern should also be measured in cooked fruits and vegetables (and in the boiled water that might be used in further cook). In particular, pesticides such as carbamates, amides, ureas, thiocarbonyl and those containing imino groups may be readily hydrolyzed in the presence of trace amounts of acid and/or base during heating or boiling. On this topic, a substantially amount of work (Chavarri et al., 2005; Kontou et al., 2004a; Kontou et al., 2004b; Knio et al., 2000) has been published on the fate of pesticide residues of dithiocarbamates and the more toxic ETU that during cooking concluding that during cooking dithiocarbamates may be converted to ETU by a factor of 30-48%. Although, ETU residues during boiling may pass into the boiling water, a significant amount remains in the processed food.

#### 4.6 Grain milling

Cleaning, conditioning and grinding are the three basic steps in grain milling process that break its grain in three main parts: wheat germ, bran and endosperm. In most studies on the distribution of pesticide residues (chlorpyrifos methyl, pirimiphos methyl, malathion, isomalathion, fenitrothion) during grain milling, the pesticide residues levels in bran are consistently higher than in wheat, usually by a factor of about 2-6 (Balnova et al., 2006; Uygun et al., 2005). Furthermore it has been reported that a considerable part of the insecticides is distributed in the semolina fractions. The residues of chlorpyrifos-methyl and pirimiphos-methyl determined in semolina were only slightly lower than the residues in bran and were, respectively, 2.0-3.6 and 1.3-3.2 times as high as those on the whole grain.

Uygun et al. (2008) reported that the carryover percentage of malathion from wheat to semolina was 16-28%, of fenitrothion 17-22%, of chlorpyrifos methyl 7-8% and of pirimiphos methyl 23-28%. As already reported for grain storage, pesticides are retained on the seed coat and tend to concentrate to the bran and germ which contain high levels of triglycerides and in consequence the lipophilicity of the pesticide residue on the processed grain may forecast its fate in the processed food product during grain milling. In conclusion Kow may adequately explain the different reductions of different pesticides that have been reported in wheat through milling; the reduction of malathion and fenitrothion was about 95%-100%, (Uygun et al., 2005), the reduction of deltamethrin was about 57.6% (Marei et al., 1995) in wheat through milling to flour.

#### 4.7 Oil Production

Vegetable oils and fats are extracted from a variety of fruits, seeds, and nuts. Depending on the RAC, the preparation of raw materials may include husking, washing, crushing or other conditioning. The oil extraction processes are generally mechanical (boiling and/or centrifugation for fruits, pressing for seeds and nuts) or involve the use of solvents such as hexane. After boiling, the liquid oil is skimmed; after pressing, the oil is filtered; and after solvent extraction, the crude oil is separated and the solvent is evaporated and recovered. The solid by-products of oil processing usually are conditioned (for example, dried) and are reprocessed to yield other products such as for animal feed, soil amendments, food additives and soaps. The produced crude oil before its consumption is often being subjected to a refining process to remove undesirable compounds that contribute undesirable colour, flavours and aromas which are disagreeable to consumers, affect the stability of the product and/or are toxic in nature. Oil refining includes degumming, neutralization, bleaching and deodorization.

Although most pesticide residues are not affected significantly by the washing procedure of fatty RAC, residues in oil-seeds following husking are very low or non-detectable as it has been reported in relative studies from field applications (Holland, 1994). However, the following oil extraction processes by means of either mechanical or chemical (solvent extraction) have high theoretical concentration factors (from 2.3 for coconut oil to 1000 for citrus oil) (EPA, 1996) and the fate of pesticide residues during edible oil production is of great importance.

##### 4.7.1 Fate of pesticides in unrefined, edible vegetable oil

Olive oil is the more important vegetable oil in European Market and the more characteristic unrefined vegetable oil that could be characterized as "*virgin*" according to the process of its extraction. The extraction process of unrefined olive oil involves the washing and milling of the fruit, the malaxation of the produced olive paste by slow mixing at a constant temperature (usually below 30°C) for 30-90 min and the separation of oil by a press or a decanter (centrifugation system). Depending on the processed olives (variety and degree of maturation) and the decanting extraction technology used, additional water may be added during malaxation and centrifugation processes to better separate oil and increase oil yields. The theoretical processing factors of virgin olive oil by this process range widely (usually range from 4-6) depending on the variety of the olive fruits (oil and water content) and the decanting extraction technology used for oil extraction (Amvrazi & Albanis, 2009; EC, 2005). However, water soluble pesticides such as acephate, dimethoate, methamidophos,

omethoate and phosphamidon pass into the aqueous phase during the extraction of oil from olives (Amvrazi & Albanis 2008; Cabras et al., 2000; Cabras et al., 1997; Letza-Rizos & Avramides, 1995; Leandri et al., 1993; Ferreira & Tainhan, 1983) and only a small percent is transferred into the oil (e.g. 6.3-8.8% for dimethoate) depending on the water content during the extraction of the olives (Amvrazi & Albanis, 2008). Other pesticides with lower water solubilities (azinphos methyl, buprofezin, chlorpyrifos, fenthion, deltamethrin, diazinon, endosulfan, quinalphos,  $\lambda$ -cyhalothrin, methidathion, parathion methyl) were found to concentrate in the oil with a concentration factor of 2-7 (Amvrazi & Albanis 2008; Cabras et al., 2000; Cabras et al., 1997; Letza-Rizos & Avramides, 1995; Leandri et al., 1993; Ferreira & Tainhan, 1983) depending on the Kow of the pesticide residue, the oil yield of the extraction procedure and the stability of the pesticide towards volatilization, and hydrolytic and other degradative processes that might take place during the malaxation stage of the procedure. The formation of fenthion sulfoxide during olive oil production was calculated ~5% of the initial fenthion and was correlated with the water addition during oil production process. However, the formation of endosulfan sulphate was not related with the water in oil extraction process (Amvrazi & Albanis, 2008).

#### 4.7.2 Fate of pesticides in refined, edible vegetable oil

During refining process of crude oils most organochlorine and organophosphorous pesticides in edible vegetable oils can be reduced considerably (concentration factors <0.1), but pyrethroid pesticides remain to a certain extent (Fukazawa et al., 1999; Hilbert et al., 1998; Zayed et al., 1998; Miyahara & Saito, 1993; Wolff, 1974). From the four main processes of crude oil refining (degumming, neutralization, bleaching and deodorization), deodorization is the process that eliminates pesticide residues the most in the final product. Although neutralization with alkali is not expected to affect organochlorines and pyrethroids in the refining process (Fukazawa et al., 1999; Hilbert et al., 1998), it has been reported that organophosphates may be reduced by 28-50% during alkali refining of fortified olive oil (Morchio et al., 1992).

The bleaching step is common for both physical and alkali refining and concerns the decolouration and the removal of undesirable compounds through absorption. The usual material is fuller's earth or carbon and charcoals materials in combination with fuller's earth. For optimum adsorption of most undesirable components to be achieved, the reaction time usually ranges from 15 - 30 min at 90°C. In the field of pesticides, it has been reported that bleaching by activated earth is not affecting significant most pesticide residues transferred in crude oil from RAC. However, it has been reported that endrin (Vioque et al., 1973) and simazine (Ruiz Méndez et al., 2005) have been completely eliminated in bleached oil. Zayed et al. (1998) reported carbofuran elimination at 20 % during bleaching with Fuller's earth at 80-100°C for 10 min and Morchio et al. (1992) reported that during decolorization, the percentage reduction of different organophosphates (dimethoate, diazinon, cis- and trans phosphamidon, parathion methyl, malathion, fenthion, and methidathion) varied from 95% (diazinon) to 30% (methidathion).

Deodorizing of oils and fats consists mainly of steam distillation under vacuum. During deodorization residual free fatty acids, aldehydes and ketones that constitute the volatile, taste and odour components are being removed from crude oil. Pesticides as well as other contaminants such as the lower molecular weight, poly aromatic hydrocarbons (PAHs) could be significant eliminated at this point (Ruiz Méndez et al., 2005; Cejpek et al., 1998; Hilbert et al., 1998; Morchio et al., 1992; Vioque et al., 1973). However, although Morchio et

al. (1992) reported the complete elimination (95%) of organophosphates in refined olive oil, Hilbert et al. (1998) found that the deodorizing step decreased the amount of the most volatile organochlorine contaminants ( $\alpha$ -hexachlorocyclohexane, lindane, hexachlorobenzene) to below the detection limit (5 $\mu$ g/Kg) whereas concentrations of the less volatile organochlorine pesticides (dieldrin, p,p'-Dichlorodiphenyl dichloro ethylene, p,p'-1,1-dichloro-2,2-bis(p-chlorophenyl) ethene) and polychlorinated biphenyl were reduced to ~50% of the initial concentration in the crude fish oil. Ruiz Méndez et al. (2005) also reported the complete elimination of simazine, endosulfan, oxyfluorfen and diflufenican during deodorizing step of the physical refining process of olive oil at 260°C. During the refining process of soybean oil to which had been added 9 pyrethroid pesticides (pyrethrins, cyhalothrin, deltamethrin, permethrin, cypermethrin, cyfluthrin, fluvalinate, fenvalerate and flucythrinate, 5 mg/kg each) all pesticides remained for the most part in the oil during degumming, alkali-refining and bleaching. During deodorization at 260 °C, pyrethrins remarkably decreased, while the amounts of cyhalothrin, deltamethrin, permethrin, cypermethrin and cyfluthrin were reduced by ~50%. Only slight decrease was noted in fluvalinate, fenvalerate and flucythrinate under the same conditions.

#### 4.8 Drying

Drying of RAC could be performed by the sun or a food dryer or in an oven. The different drying processes have different effects on pesticide residues on RAC since sun light may additionally photodegrade pesticide residues. Although the loss of water leads to increased theoretical processing factors during drying the respective factors of pesticide residues in dried food are generally lower.

Thus, although dried apricots have a theoretical processing factor ~5-6, specific pesticide residues (bitertanol, diazinon, procymidone, iprodione, omethoate, ziram) in dried apricots have been detected at lower levels as compared with raw fruits (Cabras et al., 1998b; Cabras 1997a). However under the same conditions of drying, fenitrothion disappeared completely, dimethoate did not change; phosalone was tripled whereas omethoate and ziram almost doubled (Cabras et al., 1997a). No changes among residues of bitertanol, diazinon, procymidone and iprodione were observed among pesticides studied with the two different drying procedures (oven and sundrying) tested, except of phosalone that doubled after sun drying (tripled by oven drying) in the processed apricots. Similar results have been reported for resin processing. Although the theoretical processing factor of resins is ~4, pesticides processing factors ranged from 0.08-1.7 for benalaxyl, dimethoate, iprodione, metalaxyl, phosalone, procymidone, vinclozoline, and cypermethrin (Lentza-Rizos & Kokkinaki, 2001; Cabras et al., 1998b). In a further study concerning the mechanisms occur during oven drying, the decrease of dimethoate was attributed to heat, of benalaxyl, procymidone and phosalone to co-distillation and of iprodione and metalaxyl to the combined action of heat and co-distillation (Cabras et al., 1998b). Furthermore, the type and the variety of the processed RAC may play a significant role on the fate of pesticides during drying; the higher the surface to-weight ratio, the more effective the loss.

#### 4.9 Alcoholic beverages production

##### 4.9.1 Wine making

The winemaking process begins with the pressing of the grapes by forming a biphasic system made up of the must (an acid aqueous liquid phase with pH 2.7-3.7) and the pomace (a solid phase which contain cake and lees). The following step is fermentation and this

process can be carried out either with or without grape skins. In the former case (with maceration) the wine will be made with all of the residues on the grapes; in the latter case (without maceration) the process will include only the residues that have passed in the must. The grape pomace (cake and lees) is the main by-product from winemaking and traditionally has been used to produce pomace brandy (or marc brandy), and grapeseed oil. Today, it is mostly used as fodder or fertilizer.

The fate of pesticide residues on grapes during winemaking has been widely studied. In most reported data, pesticide residues present on grapes (i.e. diniconazole, famoxadone, fenbuconazole, flufenoxuron, flusilazol, lufenuron, teflubenzuron, trifloxystrobin) remain adsorbed in the cake and lees (which are by-products of wine-making) at relevant levels, and are transferred to the wine in low percentages after fermentation depending, mainly on the initial partition of a pesticide residue between the must and the cake and lees (Likas, 2009; Likas & Tsiropoulos, 2009; Calhelha et al., 2006; De Melo Abreau et al. 2006; Tsiropoulos & Likas, 2005; Tsiropoulos et al., 1999). Azoxystrobin, benalaxyl, benomyl, dimethoate, fenhexamide, iprodione, metalaxyl-m, methidation, procymidone, pyrimethanil, spiroxamine and tebufenozide are several pesticide residues that have been reported to be transferred from the grapes to the wine at relevant amounts (20-30% for all pesticides but benomyl that transferred 100%) (Likas, 2009; Cabras & Angioni, 2000).

However, the partition coefficient of a pesticide residue between the solid pomace phase and the liquid phase of must that mainly depend on the  $K_{ow}$  and water solubility of the pesticide is not the only parameter that defines pesticides fate during wine-making. Dichlofluanid (Calhelha et al., 2006; Cabras & Angioni, 2000), chlozolinate (Gennari et al., 1992), folpet, captan (Angioni et al. 2003), thiazinan, mepanipyrim and chlorpyrifos (Cabras & Angioni, 2000) are some of the pesticide residues that their dissipation in the final produced wine has been attributed the pesticide degradation from the time of pressing and during fermentation. Yeasts that usually are being used in vinification processes have shown the ability to degrade some pesticides belonging to the pyrethroid and thiophosphate classes (chlorpyrifos-methyl, fenitrothion, parathion, quinalphos). Moreover, yeasts adsorb some pesticides, thus contributing to their removal from the wine at the end of fermentation (Cabras & Angioni, 2000).

#### **4.9.2 Pomace brandy preparation (distillation)**

Pomace brandy is the liquor distilled from cake, lees (grape pomace) and/or wine. Since, grape pomace that contains most of the pesticide residues present on grapes, is the main raw material for pomace brandy production, residues are expected to be transferred in the final alcoholic beverage. However, although, the theoretical concentration factors of pesticide residues on grapes during the pomace brandy preparation process have been calculated to range from 10 to 574 (Cabras et al., 1997b), pesticide residues do not concentrate in the final edible product, mainly because of their moderate volatility that disables their transfer through distillation. In relative reported studies performed in laboratory scale processes no detectable residues of fosetyl aluminium, fenarimol, methidathion, myclobutanil, iprodione, metalaxyl, triadimefon, parathion methyl and dimethoate were detected in the final-distilled spirits of wine, whereas vinclozolin, fenthion, quinalphos and benalaxyl were transferred to the final spirits at very low percentages (0.1-2% from lees and 5-13% from wine). That remarkable decrease in residues during the distillation process could depend on fact that very low amounts of residue are transported

by alcoholic vapors while higher amounts are transported by water vapors (Cabras & Angioni, 2000; Cabras et al., 1997b).

#### 4.9.3 Beer production (malting)

In general during beer production, pesticide residues that might be present on barley and hops are transferred in beer according to their *K<sub>ow</sub>*. Water soluble compounds are more likely to be transferred into the beer whereas the more lipophilic are retained in the lipophilic trub and/or are metabolized by the biotic metabolism of the added yeast and/or degraded by abiotic processes from the relative reductive environment, during fermentation. In practice, a combination of the malting process, the high dilution with water and the filtering processes generally result in non detectable residues in beer.

Malting of barley resulted in loss of about 80% of fenitrothion residues (Holland 1994), 58% of tebuconazole, 48% of fenarimol, 22-23% of Z- and E-dimethomorph, and almost diminished residues of chlorfenapyr, quinozifen and pyridaben (Hengel & Shibamoto 2002). Synthetic pyrethroid residues underwent similar high losses during malting (Holland 1994). However, in the final produced beer dimethomorph residues were detected at about 0.31% of original levels on hops (tebuconazole, fenarimol, chlorfenapyr, quinozifen and pyridaben were not detected), glyphosate residue levels in beer were about 4% of original levels in the barley (JMPR, 1987), monocrotophos at lower than 1% of the original concentration (JMPR, 1972), and myclobutanil at lower than 0.009 (JMPR 1998).

## 5. Conclusions

Literature review presented in this chapter demonstrated large differences among the different pesticide residues persist in or on RAC and among the different food preparation processes studied. The largest reductions in residue levels of almost all common classes of pesticides were noticed through peeling (70-100%), juicing (73-91%), and alcoholic beverages production (most pesticides were reduced at 70-100%) and the lowest through washing (22-60%) with tap water. Grain milling and drying processes could reduce pesticides at relevant percentages (58-100% and 57.5-98% respectively) and attention should be paid for pesticides with high *K<sub>ow</sub>* in grain milling and for thermally stable pesticides during oven drying. Furthermore, special concern on residues levels in the final product should be taken in unrefined oil production since pesticides reduction is low for most fat soluble pesticides (35 - 78%) and processing factors range from 2 to 7. Similar considerations should be taken on pesticides residues in ready to eat food after cooking since their reduction after cooking may vary widely among the different pesticides and among the different cooking procedures (especially with or without water addition through heating) studied. The study on published data presented in this chapter pointed the selective reduction of pesticides tentative to hydrolysis (acid catalyzed mainly), heat degradation and enzymatic degradation mechanisms through cooking.

Current literature on metabolites that may be formed during storage and food processing is limited and more toxic metabolites than parent compounds with critical physicochemical processes according to the mechanisms described in this chapter in the different food preparation process should be studied for their fate in the final edible products (e.g. acid sensitive pesticides as ETDC in tomatoes after comminution and mild cooking; oxon metabolites of organophosphorous pesticides after washing of RAC with ozonated water

and juicing; oxon metabolites in vegetable soups and others). This future scope is very important and of great priority to have a complete conclusion summary of the pesticides fate after the different handling of food processing technology. Results would further enable research on health risk characterization from realistic dietary exposures to pesticide residues; enable the settlement of MRLs or processing factors for pesticide residues in food products, and further enable the optimization of food technology processes with regard to pesticide residues dissipation.

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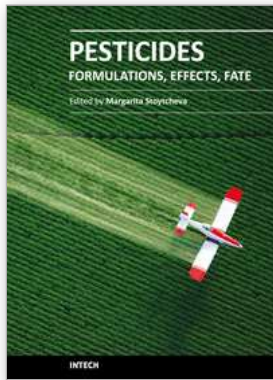


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## **Pesticides - Formulations, Effects, Fate**

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This book provides an overview on a large variety of pesticide-related topics, organized in three sections. The first part is dedicated to the "safer" pesticides derived from natural materials, the design and the optimization of pesticides formulations, and the techniques for pesticides application. The second part is intended to demonstrate the agricultural products, environmental and biota pesticides contamination and the impacts of the pesticides presence on the ecosystems. The third part presents current investigations of the naturally occurring pesticides degradation phenomena, the environmental effects of the break down products, and different approaches to pesticides residues treatment. Written by leading experts in their respective areas, the book is highly recommended to the professionals, interested in pesticides issues.

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