**Efficacy of electrolyzed water, chlorine dioxide and photocatalysis for disinfection
and removal of pesticide residues from stone fruit**

Hector Calvo^a, Diego Redondo^b, Sara Remón^a, María E. Venturini^{a*}, Esther Arias^c

^aGrupo de Investigación de Alimentos de Origen Vegetal, Instituto Agroalimentario de Aragón-IA2-(Universidad de Zaragoza-CITA), C/Miguel Servet 177, 50013 Zaragoza, Spain

^bNutrición de Cultivos Frutales, Estación Experimental Aula Dei-CSIC, Avda. Montañana 1005, 50059 Zaragoza, Spain.

^cParque Científico Tecnológico Aula Dei, Avda. Montañana 930, 50059 Zaragoza, Spain

***Corresponding author:**

Maria E Venturini, Grupo de Investigación de Alimentos de Origen Vegetal, Instituto Agroalimentario de Aragón-IA2-(Universidad de Zaragoza-CITA), C/Miguel Servet 177, 50013 Zaragoza, Spain.

E-mail: ugeventu@unizar.es

Abstract

Concerns about chemicals and pesticides in food plants have increased dramatically during the last decade. Following stricter legislation and studies about toxicity and human health risks, new ways of reducing toxic residues are urgently required. In this study, oxidizing agents such as electrolyzed water (EW), chlorine dioxide (ClO_2) and photocatalysis have been used during the postharvest phase in order to remove the residues of cyprodinil, tebuconazole and iprodione from the surface of peaches, nectarines and apricots. Moreover, the disinfection capability of these agents has also been tested as an alternative to sodium hypochlorite. Our results show that pesticide removal from stone fruits by oxidizing technologies significantly varies depending on the treatment used and the target substance. ClO_2 significantly reduced tebuconazole residues from all the fruits (by more than 60 %) and photocatalysis similarly reduced iprodione residues (between 50 and 70 %). However, EW achieved a percentage of residue reduction similar to that of tap water, never exceeded 40 %. In contrast, EW reduced the superficial microbiota to undetectable counts, also decreasing the percentage of rotted fruit from 32 to 7 %. Photocatalysis produced similar results since it was able to decrease the microorganisms present on the fruit surface by nearly 2 log units and the incidence of disease by 50 %. It was concluded that a strategy combining photocatalysis treatment during cold storage to reduce pesticide residues and spoilage microorganisms with electrolyzed water washing to reduce any remaining microbial contamination prior to commercialization will substantially reduce disease and ensure the safety of stone fruits for human consumption.

Keywords: oxidizing technologies, pesticide residues, microbial decontamination, postharvest rots

1. Introduction

A large number of pesticides are applied in agricultural areas all over the world. The worldwide pesticide consumption (except Northern America) reported by FAOSTAT was 3,013,970 tons of active ingredients in 2014 (Cengiz et al., 2017). As a consequence of their widespread use, they have become serious food contaminants, posing a threat to human health. Considerable laboratory studies and epidemiological evidence show that certain pesticides are related to carcinogenesis, endocrine disruptions, birth defects, reproductive disorders and cardiovascular diseases (Mostafalou and Abdollah, 2013). Therefore, a risk assessment is necessary to ascertain the health effects due to intakes of pesticide residues on food (Chen and Zhu, 2011). To reduce possible health risks from pesticides, decreasing their residues, especially in widely consumed food commodities, is crucial. Fresh fruits and vegetables are the major food source for pesticide exposure. The reason is that fresh produce accounts for about 30 % of an individual diet by mass and is assumed to contain traces of residual pesticides as much of it is consumed raw (Cengiz et al., 2017).

Stone fruits are some of the most widely grown and consumed fruit in the world. In 2016, Spain exported 999,981 t of peach, nectarine, plum, apricot and cherry with a total value of €1 billion (Federation of Fruit, Vegetable, Flower and Live Plant Grower Exporter Associations (FEPEX, 2016)). Given their high economic value, it is necessary to obtain high-quality crops and fruits in order to maintain Spanish exports. Cyprodinil, iprodione and tebuconazole are widely employed during the cultivation of stone fruits. Cyprodinil [4-cyclopropyl-6-methyl-N-phenylpyrimidin-2-amine] is an anilinopyrimide also with a systemic and broad-spectrum fungicide action. It also has a low water solubility (13 mg L⁻¹ at 20 °C) and volatility (5.1 x 10⁻⁰¹ mPa at 20 °C) (PPDB), and is unlikely to leach to groundwater. In soils it is moderately persistent, although this usually

depends upon local conditions, and it is likely to degrade quickly in daylight. The dicarboximide iprodione [3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide] has both preventive and curative antifungal activity and is also broad-spectrum. It inhibits the germination of spores, cellular division and mycelial growth. It remains in the soil for approximately 50-160 d. Its water solubility (6.8 mg L^{-1} at 20°C) and volatility ($5.0 \times 10^{-4} \text{ mPa}$ at 20°C) are also low. Tebuconazole [(RS)-1-p-chlorophenyl-4,4-dimethyl-3-(1H-1,2,4-triazol-1-ylmethyl) pentan-3-ol] is a broad-spectrum systemic fungicide belonging to the triazole class, used on grapes, cereals, stone fruits, peanuts, bananas and other fruits. It is rapidly absorbed into the vegetative parts of the plant, with principally acropetal translocation, to inhibit ergosterol biosynthesis by fungi (Lucini and Molinari, 2008). It has a low water solubility (36 mg L^{-1} at 20°C) and volatility ($1.3 \times 10^{-3} \text{ mPa}$ at 20°C) (PPDB, Pesticide Properties Data Base). The chemical structures of these pesticides are shown in Figure 1. According to the European Legislation on Maximum Residue Limits (MRL) (Commission Regulations (EU) 400/2015 and 626/2017), tebuconazole, cyprodinil and iprodione are registered for use on stone fruits in Europe with MRLs (mg kg^{-1}) of 0.6 (apricots and peaches) and 1 (sweet cherries and plums), 2.0 for all stone fruits, and 3.0 (plums), 6 (apricots) and 10 (sweet cherries and peaches), respectively.

Figure 1. Molecular structures of the pesticides tebuconazole, cyprodinil and iprodione.

Fresh produce harvested from the fields must be safe and new alternatives for removing pesticide residues need to be developed and evaluated. Although some oxidation technologies are increasingly efficient for pesticide degradation, a series of transformation products (TPs) with unknown physical-chemical properties may be produced before the parent compounds are completely mineralized. Numerous studies have reported that various TPs have more polarity, toxicity or persistence than the parent itself, which suggests the TPs may carry an environmental risk (González-Rodríguez et al., 2011; Sharma et al., 2014; Xu et al., 2014; Nicol et al., 2016). Thus, apart from their effectiveness, the toxicity of the degradation products from the parent compounds, if they are likely to be formed, is probably the key factor for deciding whether a process is appropriate for a certain application.

After harvest, fresh produce is often washed with tap water to remove dirt and debris and to reduce microbial counts but this washing has limited effects on pesticide residue removal because many pesticides are hydrophobic (Iizuka and Shimizu, 2014). Water is a useful tool for reducing potential contamination but its disinfection is necessary to maintain its microbial quality, avoiding cross-contamination between clean and contaminated products. The fruit and vegetable industry has used chlorine as one of the most effective sanitizers to assure the safety of its products, sodium hypochlorite (NaOCl) being the most commonly used source of chlorine. Several studies have demonstrated the efficacy of chlorine in degrading pesticides (Pugliese et al., 2004; Duirk et al., 2009; Hao et al., 2011). Recently, Qi et al. (2018) established that electrolyzed oxidizing (EO) water, as an advanced chlorine-based solution, is superior to regular sodium hypochlorite-based sanitizers in removing pesticide residues from fresh produce. Therefore, given that there are many studies that support its antimicrobial activity on different fruits (Graca et al., 2011; Torlak, 2014; Ding et al., 2015) and vegetables (Ding et al., 2011; Gómez-López

et al., 2013; Hao et al., 2015; Mansur and Oh, 2015), it is of great interest to investigate its efficacy in degrading pesticides.

Washing solutions with the addition of strong oxidizing agents such as ozone (Ong et al., 1996; Hwang et al., 2001; Wu et al., 2007; Chen et al., 2013) or chlorine dioxide (Hwang et al., 2001; Hwang et al., 2002) have also been shown to be effective in removing residual pesticides from produce samples. In recent years, chlorine dioxide (ClO_2) has gained attention as an alternative disinfectant to NaClO for the fresh and fresh-cut produce industry (Artés et al., 2009, Gómez-López et al., 2009, Van Haute et al., 2017). ClO_2 is highly effective for the preservation of products such as carrots (Gómez-López et al., 2008), tomato (Guo et al., 2014), strawberry (Trinetta et al., 2013) and blueberry (Sun et al., 2014). ClO_2 oxidizes but, unlike chlorine, it does not chlorinate and, as such, chlorinated disinfection by-products (DBPs) are not significantly produced (López-Gálvez et al., 2010; Tomás-Callejas et al., 2012). However, when ClO_2 oxidizes water matrix constituents, it is reduced principally to chlorite (ClO_2^-) and, to a lesser extent, to chlorate (ClO_3^-) and chloride (Hua and Reckhow, 2007). ClO_2^- and ClO_3^- can cause anaemia in some animals and high levels are harmful to the thyroid function (Hebert et al., 2010). ClO_2^- are classified as noncarcinogenic products but are regulated DBP in the United States at a maximum level of 1 mg L^{-1} in drinking water (United States Environmental Protection Agency (USEPA), 2009). ClO_3^- is a substance that is no longer approved as a pesticide according to the European Commission Decision 2008/865/EC (EC, 2008) but no specific MRLs have been established and, therefore, a default MRL of 0.01 mg kg^{-1} is applicable. The EFSA Panel on Contaminants in the Food Chain (EFSA, 2015) reported that the source of the chlorate residues detected in food could arise from the use of chlorinated water for food processing and the disinfection of food processing equipment. Gil et al. (2016) made some practical recommendations to minimize the

chlorate accumulation in the water washing process and the residues found in fresh cut lettuce when sodium hypochlorite was used as a washing aid, for example using a more diluted chlorine solution and shorter storage times of the stock solution, together with proper rinsing. Chen et al. (2011) did not detect ClO_2 , ClO_2^- , or ClO_3^- residues in mulberry fruits treated by $60 \text{ mg L}^{-1} \text{ ClO}_2$ for 15 min and attributed this effect to the potable water rinse applied after treatment. However, data on the transfer of ClO_2^- and ClO_3^- to any specific commodity is needed before ClO_2 can be recommended as a water washing treatment.

Radiant catalytic ionization (RCI) or photocatalysis stands out among recently developed advanced oxidation processes (AOP). The technology of RCI is still not well known, but its popularity is gradually increasing. It uses the appropriate wavelength and the phenomenon of photooxidation in the presence of UV radiation and appropriate photo-catalysts such as TiO_2 . This leads to the production of superoxide ions and hydroxides, and the generation of plasma based on hydrogen peroxide (Skowron et al., 2018). This process involves the generation of the free hydroxyl radical ($\bullet\text{OH}$), a powerful and non-selective chemical oxidant (Heponiemin and Lassi, 2012). Generally, the reaction of hydroxyl radicals and organic compounds will produce water, carbon dioxide and salts. However, the attack of the $\bullet\text{OH}$ radical in the presence of oxygen generates a complex series of oxidation reactions in which the exact routes of these reactions to complete mineralisation of the organics are still not quite clear. The advantage of this technology is the ability to perform constant disinfection of the ambient air in food processing plants (Skowron et al., 2018). RCI uses very low levels of ozone and in the catalytic process breaks ozone down forming other oxidation products.

In this study, the objective was to evaluate the effectiveness of three oxidizing technologies (electrolyzed water, chlorine dioxide and photocatalytic process) in

removing the widely used pesticides cyprodinil, iprodione and tebuconazole from stone fruits (peach, nectarine and apricot) as well as their antimicrobial disinfectant efficacy. Moreover, the impact of the treatments on the physico-chemical quality of the products was investigated. To our knowledge, this is the first study where EW, ClO₂ and photocatalysis have been applied for the removal of these pesticide residues from fresh stone fruit.

2. Materials and methods

2.1. Fruit samples

The experiment involved 60 trees randomly selected from an experimental orchard in the Campus of Aula Dei, Montañana (Aragón, Spain) located 10 min from our laboratory. All were organically grown and it was ascertained that the samples were not initially contaminated with residues. The absence of pesticide residues was verified by chromatographic analysis. For each species, peaches (cv. Spring Flame), nectarines (cv. Nectafun) and apricots (cv. Pink Cot), fruits of similar size, colour and an absence of any defect were randomly and manually picked and transferred immediately to the laboratory. There, they were cooled from approximately 20-23 °C down to 4 °C in approximately 150-200 min by forced air. Fruit were stored at 1 °C and used for experiments within 4 days of collection. Prior to the decontamination trials 25 fruits were used for measurement of the total soluble solid contents, pH, titratable acidity and firmness. Table 4 shows a physico-chemical description of the different fruit species.

2.2. Chemicals and standards

Commercial tebuconazole, Genius 25 WG (Exclusivas Sarabia, Alpicat, Spain), iprodione, Iprodione 50 Flow (Fitoloma S.L., Jaén, Spain), and cyprodinil, Chorus 50 WP

(Syngenta, Basel, Switzerland) were used for the preparation of dipping solutions. Stock solutions of the commercial pesticides were prepared by mixing with water according to the manufacturers' instructions. The preparation of the pesticide solutions was performed in a well-ventilated fume hood. Protective gloves were worn during the handling, mixing and transportation of the solutions.

2.3. Oxidizing treatments: preparation, dosing and monitoring

The electrolyzed water (EW) equipment used during this study was a DiaClean® Lab Unit (WaterDiam Sarl, Delémont, Switzerland) fitted with boron-doped diamond on silicon (BDD/Si) electrodes. This equipment is able to produce electrolyzed oxidizing water, so by changing its potential (V) it is possible to obtain several active compounds such as •OH radicals. The water was previously acidified with 80 mg L⁻¹ citric acid (Sigma–Aldrich) until pH 6.5 and with 1 g L⁻¹ of NaCl (Panreac Química, Barcelona, Spain) to obtain greater free chlorine and ORP as well as more radicals with higher oxidant activity. Subsequently, the equipment was operated for 1 hour under a coupled refrigerating system (0-2 °C) in order to keep the water cold. Control of the chemical properties of water such as the pH, ORP and free chlorine is necessary during and after EW production. A pH and redox multimeter (Crison, Barcelona, Spain) and photometer (HI 83099 and kit HI 93701-0, Hanna Instruments, Padova, Italy) were used for this purpose. A stabilized liquid formulation of ClO₂ (7500 mg L⁻¹) were diluted to reach a final concentration of 10 and 20 mg L⁻¹. All solutions were prepared immediately prior to use and the temperature, pH, chlorine and ORP were monitored during the application. The photocatalysis unit was installed in a laboratory cool chamber with capacity of 8.40 m³ and ensuring an air flow rate of 6 m s⁻¹. The physicochemical characteristics of the wash water used for each treatment can be seen in Table 1.

Table 1. Physicochemical characteristics of the process wash waters used in the different treatments.

Washing treatments	Active agent	Active agent concentration (mg L ⁻¹)	pH	ORP (mV)
Tap water	-	-	6.4	150
Sodium Hypochlorite (SH)	Free chlorine	3.7	6.7	730
Electrolyzed Water (EW) + NaCl	Free chlorine	165	6.7	775
Chlorine dioxide (ClO ₂)	Chlorine dioxide	10	6.4	740
	Chlorine dioxide	20	6.5	760

2.4. Experimental design

In the pesticide reduction assays, the fruits were immersed in the pesticide solutions in accordance with the procedure described by Iizuka and Shimizu (2014). Doses of 5 g L⁻¹, 2 mL L⁻¹ and 0.7 mL L⁻¹ were prepared for cyprodinil, iprodione and tebuconazole, respectively. These doses were selected according to the manufacturer's data sheets being in the range recommended for stone fruit field applications (3.0-7.5 g L⁻¹ for cyprodinil, 1.5- 2.3 mL L⁻¹ for iprodione and 0.5-0.75 mL L⁻¹ for tebuconazole). Fruits were soaked for 10 min in 50-liters buckets containing each commercial pesticide solution and stirred every minute, followed by natural drying at room temperature for 1 hour. After that, the samples were completely submerged for 5, 15 and 25 min in a 50-liter bucket containing the respective treatment solutions (EW or ClO₂ (10 and 20 mg L⁻¹)). At each control time 5 fruits were extracted from the solution and natural drying at ambient temperature for 1 h. After that, the analysis of pesticide residues, as detailed in section 2.5, were carried out. The initial concentrations of fungicides (mg kg⁻¹) in peaches, nectarines and apricots were, respectively, 20.74 ± 2.27, 12.52 ± 0.87 and 13.61 ± 1.36 for cyprodinil, 26.11 ± 1.30, 19.73 ± 2.36 and 25.94 ± 3.11 for iprodione and 7.05 ± 0.45, 6.32 ± 0.44 and 7.65 ± 1.07 for tebuconazole. Treatments with tap water for 5, 15 and 25 min were also included as control. All the experiments were conducted in precooled water (2 °C). Process temperature was controlled by pumping cold water through stainless steel

heat exchangers immersed in the process water to never exceed 5 °C. In the case of photocatalysis, the contamination procedure was the same but after drying the fruits were placed in a cold chamber with the photocatalytic unit installed. The analysis of pesticide residues were carried after 15 d at 1 °C, an average storage time for this fruit species.

The antimicrobial efficacy of EW and ClO₂ washing treatments was tested in the same conditions as described above, but only 5 and 15 min-treatments were applied since longer times are difficult to apply in a fruit and vegetable packing centre. A batch washed with a sodium hypochlorite (SH, 100 mg L⁻¹) solution for 5 min was included as a reference disinfection treatment and another treated with tap water was used as control. In these experiments the decontaminating step was followed by rinsing in running tap water for 1 min and by natural drying at room temperature for 1 h. Then, microbial analysis, as detailed in section 2.6., were carried out. In the case of photocatalysis, the reduction of the epiphytic microbiota were studied only in peaches after 15 d of storage at 1 °C in a cold chamber with the photocatalytic unit installed.

The influence of the EW (5 and 15 min) and ClO₂ (15 min) washing treatments on the incidence and severity of rots were also studied. In this case, also only peaches (cv. *Spring Flame*) were employed. Peach was selected as model fruit for these experiments since, within the fruits analysed, has longer storage periods and rots are more likely to occur. Unwashed fruit was used as control and sodium hypochlorite as a reference disinfection technology. The washing treatments were applied in the same conditions as described above. After rinsed with tap water, the fruit was left to dry for 1 h and stored at 1 °C for 15 d followed by 10 d at 22 °C and 85 % R.H in order to simulate an ordinary period of postharvest storage and commercialization. For the photocatalytic treatment the fruit rot incidence was established after 15 d at 1 °C in the photocatalysis unit followed

by 10 d at 22 °C and 85 % R.H in a conventional chamber. Twenty-five fruits per treatment were monitored.

In parallel to the studies of removal of pesticide residues and disinfection, and to evaluate whether the application of the oxidation technologies produced changes in the fresh fruit characteristics, analyses of the quality parameters (section 2.7) were performed before the treatments were applied and after a storage period of 15 d at 1 °C. In this case only the fruit washed with the maximum treatment times assayed in this study (25 min) were analyzed. For the photocatalytic treatment, the quality parameters were also evaluated after 15 d at 1 °C.

2.5. Analysis of pesticide residues on fruits

For the preparation of the samples, five units of fruit were minced in a mini food processor (Cecotec, Powerfull Titanium 1000 Full, Spain). After processing, 5.0 g of peach, nectarine and apricot separately was transferred to 25 mL vials, and 2 mL of deionized water and 3 mL of acetonitrile were added. The vials were subjected to centrifugation at 1512 g for 10 min at 4 °C. The samples were stored in a freezer at -80 °C until analysis. The freezing of the matrix and aqueous phase allowed the extraction of the organic phase with pesticides. The organic phase was collected with a micropipette and transferred to 1.5 mL glass vials for later chromatographic analysis. The presence of the tebuconazole, iprodione and cyprodinil residues in stone fruits was analyzed with a GS/MS system 7890 B (Agilent Technologies, USA). The gas chromatograph was operated in split-less mode with an injector temperature of 280 °C. The initial column oven temperature was 60 °C (1 min), with a heating range at 40 °C min⁻¹ up to 170 °C, which was maintained for 2.75 min. Another range was then applied at 10 °C min⁻¹ up to 310 °C, maintained for 20 min. Helium was used as the carrier gas with a column flow

rate of 1 mL min⁻¹. The injected sample volume was 1.0 µL and the data acquisition time was 20 min. Two HP-5ms capillary columns (Agilent Technologies, USA) of 15 m x 0.25 mm i.d. x 0.25 µm film thickness with stationary phase 5 % diphenyl/95 % dimethyl polysiloxane connected in series were used for analysis. The tebuconazole, iprodione and cyprodinil residue concentrations were calculated on the basis of the area of the integrated peaks of the samples compared with known concentrations of analytical standards of the respective pesticides. Standard curves of the three pesticides were plotted, and least-squares linear regression was performed using Microsoft Excel (Microsoft Corp., Redmond, WA) software.

2.6. Microbial analysis

The enumeration of Total Mesophilic Aerobes (TMA) and Yeasts and Moulds (YAM) was carried out by following the ISO Standards 4833-1:2013 and 21527-1:2008, respectively. The sampling was performed using a 10 cm² sterile window. Two pieces were cut from each fruit and the results were expressed as log colony forming units (CFU) per cm². Ten fruits per treatment and contact time were analysed.

2.7. Quality parameters

Firmness (F) was measured with a digital portable durometer (Durofel, Agrosta[®] 100Field). The measurement was performed on two opposite faces in the equatorial zone and firmness was expressed in Durofel Units. Soluble solids content (SSC) was measured with an Atago DBX-55A refractometer (Atago CO, Tokyo, Japan) at 20 °C and mean values were expressed in °Brix. Acidity was quantified in 25 mL of juice extracted from 200 g of fruit by potentiometric titration with 0.1 N NaOH to an end point of pH 8.2 and values were expressed in g malic acid L⁻¹. Twenty-five fruits per treatment were analysed.

2.8. Statistical analysis

All the experiments were replicated in two separated d. Means and standard deviations were calculated using Excel (Microsoft, USA). SPSS software was used for statistical analysis. A t-student test and one-way analysis of variance was conducted followed by Duncan's test with the Anova procedure. A $p < 0.05$ was considered to be significantly different.

3. Results and discussion

3.1. Pesticide removal by electrolyzed water (EW) and chlorine dioxide (ClO_2) washings and by photocatalysis treatment

Figures 2, 3 and 4 show the experimental results of pesticide degradation by EW and ClO_2 treatments after 5, 15 and 25 min washing for peach (cv. *Spring Flame*), nectarine (cv. *Nectafun*) and apricot (cv. *Pink Cot*), respectively.

The efficacies of EW for cyprodinil and iprodione removal from all the fruits were very low (about 15-20 %) and slightly higher in the case of tebuconazole (about 30 %) being the removal efficacy, in most of the cases, lower to that obtained with tap water rinsing (around 40 %). Three previous studies have highlighted the effectiveness of electrolyzed water on pesticide removal from fresh produce (Lin et al., 2006; Hao et al., 2011; Qi et al., 2018). However, all of them employed acidic or alkaline electrolyzed waters, not being comparable therefore with ours where electrolyzed water has a neutral pH that probably does not affect the stability of the tested fungicides. Many factors affect the pesticide removal rate, among others, the physicochemical properties of the pesticides (K_{ow} value, solubility and pKa) but also the physical and chemical characteristics of the cleaning solution, such as cleaning fluid temperature, pH and polarity (Radwan et al., 2005; Lin et al., 2006; Zhang et al., 2007; Kin et al., 2010; Gonzalez-Rodriguez et al.,

2011). Water-soluble pesticides are more readily removed than low-polarity materials (Burchat et al., 1998; Timme and Walz-Tylla, 2004). All the fungicides tested in our study have low solubility in water (13.0, 6.8 and 36.0 mg L⁻¹ for cyprodinil, iprodione and tebuconazole, respectively) and an octanol–water partition coefficient (log K_{ow}) of 3.5, 3.0 and 3.7, respectively, being therefore lipophilic substances that have a tendency to migrate into the wax layer on fruit surfaces which makes the pesticides less likely to come into contact with the dissolved oxidizing compounds in washing solutions (López-Fernández et al., 2013). Moreover, Pugliese et al. (2004) concluded that oxidizing treatments (hydrogen peroxide, potassium permanganate and sodium hypochlorite) was not more effective than tap water washing for pesticide residue reduction in nectarines and that the main mechanism for removing the residues was dissolution. In general, fruit vegetables that possess hydrophobic characteristic because of the waxy layer on the surfaces had worse pesticide reduction results than leafy vegetables (Lin et al., 2006). Thus, our results suggest that pesticide chemical degradation by EW was unappreciable and that the penetration of electrolyzed water into the waxy surface cuticle layers of fruit is lower than that of tap water, hindering the washing effect and producing minor reductions of cyprodinil, tebuconazole and iprodione from the surface layers of apricots, nectarines and peaches. However, the results found in the present study must not be extrapolated to other pesticides, crops or conditions.

The removal effect of ClO₂ for cyprodinil and iprodione was very similar to that of tap water, indicating that pesticide degradation did not occur and there was only a dissolution effect (Fig. 2, 3 and 4). On the other hand, ClO₂ was more effective than tap water in the elimination of tebuconazole, with pesticide removals of 64.6, 62.6 and 61.6 % for peach, nectarine and apricot, respectively. The main removal effect was detected after 15 min of washing, with no additional effect of the increasing dose or contact time.

Chen et al. (2014), studying fresh lettuces contaminated by washing in phorate and diazinon solutions at 10 mg L⁻¹, did not detect a considerable increase in the removal of pesticide residues either with the increase of the chlorine dioxide levels from 10 to 20 mg L⁻¹ or with the increase of time. The maximum reduction occurred in the first 5 min. However, when the initial pesticide solutions were at 20 mg L⁻¹, the removal of pesticides was lower but a significantly greater effect was detected with the high dose of chlorine dioxide and with longer treatment times. However, Hwang et al. (2001) did not find significant differences in the removal of mancozeb from apples at a spike level of 1 ppm between 5 and 10 ppm of chlorine dioxide but when the spike level of fungicide was 10 ppm residue levels were reduced considerably with increasing the chlorine dioxide concentration and contact time. These results suggested that the influence of the dose of chlorine dioxide and the contact time varies with the spike level of fungicide, the chemical structure and the nature of the commodity, being this last factor the main one governing the removal of residues (López-Fernández et al., 2013). This findings differs from our results since, although our inoculation doses were very high, no additional effect with increasing ClO₂ dose was observed. Probably, a substantial percentage of pesticide could have migrated into the wax layer of the fruit surface thus being inaccessible to the ClO₂ solution. Thus, ClO₂ solution at 10 mg L⁻¹ removed the maximum percentage of pesticide that can be dissolved and therefore chemically degraded. In our case, chlorine dioxide seems to partially degrade tebuconazole, having more than a rinsing effect. Regarding to the TPs of tebuconazole degraded by gaseous chlorine dioxide only one reference has been found (Wei et al., 2018). These authors proposed the tertiary butyl and p-chlorobenzyl cations caused by C–C cleavage as the degradation products of tebuconazole, but no toxicology studies were carried out so an effort to evaluate them should be done.

Figure 2. Effect of electrolyzed water (EW) and chlorine dioxide (ClO_2 , 10 and 20 mg L^{-1}) washing treatments (5, 15 and 25 min) on the degradation of 20.74 ± 2.27 , 26.11 ± 1.30 and $7.05 \pm 0.45 \text{ mg kg}^{-1}$ of cyprodinil, iprodione and tebuconazole, respectively, on peach (cv. *Spring Flame*) in comparison with tap

water. Each value is the mean of 2 replicates (5 minced fruits each) conducted on 2 separate days. Vertical bars correspond to standard deviation.

Figure 3. Effect of electrolyzed water (EW) and chlorine dioxide (ClO_2 , 10 and 20 mg L^{-1}) washing treatments (5, 15 and 25 min) on the degradation of 12.52 ± 0.87 , 19.73 ± 2.36 and 6.32 ± 0.44 mg kg^{-1} of cyprodinil, iprodione and tebuconazole, respectively, on nectarine (cv. *Nectafun*) in comparison with tap water. Each value is the mean of 2 replicates (5 minced fruits each) conducted on 2 separate days. Vertical bars correspond to standard deviation.

Figure 4. Effect of electrolyzed water (EW) and chlorine dioxide (ClO_2 , 10 and 20 mg L^{-1}) washing treatments (5, 15 and 25 min) on the degradation of 13.61 ± 1.36 , 25.94 ± 3.11 and $7.65 \pm 1.07 \text{ mg kg}^{-1}$ of cyprodinil, iprodione and tebuconazole, respectively, on apricot (cv. *Pink Cot*) in comparison with tap water. Each value is the mean of 2 replicates (5 minced fruits each) conducted on 2 separate days. Vertical bars correspond to standard deviation.

The natural decrease in the residues of fungicides in air atmosphere was low (less than 10 % in most cases) and the photocatalytic treatment significantly affected the reduction of iprodione and cyprodinil ($p < 0.05$) but not that of tebuconazole (Table 2). Among the three fungicides we assayed, iprodione proved to be the most sensitive to air photocatalysis with an overall reduction of more than 50 %, 74.3 % in the case of treated peaches. The PPDB classified iprodione as quite stable to aqueous photolysis. This pesticide is moderately persistent in soil with a half-life time of 7–60 d depending on the environmental conditions (Carmona et al., 2001). In plants, it is quickly degraded once adsorbed by the roots with the formation of 3,5-dichloroaniline as the main metabolite (Athiel et al., 1995, Lindh et al., 2007). This generated metabolite is highly nephrotoxic (Lo et al., 1990) and carcinogenic. In water, it decomposes quicker under aerobic conditions than anaerobic. Some studies have shown high persistency of this fungicide on treated fruits such as apricots (Cabras et al., 1998) and strawberries (Stensvand and

Christiansen, 2000). Karaca et al. (2012) obtained a low reduction level for iprodione inoculated in grapes exposed to 0.3 mL L^{-1} gaseous ozone (23.9 % decline after 36 d). These results showed that the oxidation-sensitive regions of iprodione such as the phenyl ring, alkyl chain and double bonds were somehow protected from oxidation by ozone. In a model system study, Hu et al. (2000) also observed a slow degradation of iprodione by gaseous (2.4 mg L^{-1}) and aqueous (0.32 mg L^{-1}) ozone treatments.

Photocatalysis for 15 d markedly accelerated the decomposition of cyprodinil with reduction rates of 33.7 %, 30.9 % and 23.2 % for peaches, nectarines and apricots. Karaca et al. (2012) did not detect any degradation of cyprodinil in table grape berries after 12 d in air and a decline of 12.2 % was found at the end of the storage period (36 d). When grapes were exposed to gaseous ozone 0.3 mL L^{-1} the residue reduction achieved was 30.6 % after 12 d of treatment and 34.7 % after 36 d, these results being very similar to ours. Anfossi et al. (2006) investigated the photoinduced degradation of 3 anilinopyrimidine fungicides (cyprodinil, pyrimethanil, and mepanipyrim). The photoproducts were very similar for the three fungicides and showed that three sites of the molecules were primarily attacked by hydroxyl radicals: the nitrogen bridge between the two rings, the phenyl ring and the pyrimidyl ring. The photodegradation of cyprodinil under UV–visible irradiation led to the formation of many transformation products by several reactions, namely direct bond cleavages, cyclization, isomerization and hydroxylation, most of the TPs being significantly more toxic than the parent molecule (Nicol et al., 2016).

In soil under aerobic conditions, tebuconazole shows moderate to medium persistence forming the soil metabolite 1,2,4-triazole which has moderate to high persistence, soil adsorption being the main route for tebuconazole dissipation. Tebuconazole is resistant to hydrolysis (half-life > 28 d or stable at pH 5, 7 and 9),

aqueous and soil photodegradation (half-life of 590 and 192.5 d, respectively) and soil metabolism (half-life of 796 d). However, it is difficult to explain the resistance of tebuconazole to photocatalysis since Stamatis et al. (2015), studying the photocatalytic degradation kinetics and mechanisms of fungicide tebuconazole in aqueous TiO_2 suspensions, concluded that the transformation of tebuconazole pathways was found to proceed through tert-butyl chain cleavage, hydroxylation, oxidation and dechlorination pathways. Scavenging experiments showed that the degradation mechanism of tebuconazole was mainly driven by $\text{HO}\cdot$ and h^+ . Finally, the application of an acute toxicity test (*Vibrio fischeri*) to selected water samples resulted in a non-inhibitory effect of the bacterial bioluminescence.

The physiochemical methods based on the production and use of hydroxyl radicals ($\cdot\text{OH}$), known as advanced oxidation processes (AOPs), have been described as effective for transforming non-biodegradable pollutants into harmless substances. However, as it has been described below, in these treatments the formation of by-products involve several photodegradation reactions, namely direct bond cleavages, cyclization, isomerization and hydroxylation. Photocatalytic air treatment has been shown to be an effective strategy for the reduction of iprodione residues in stone fruits during cold storage, but the elucidation of its degradation mechanism and the identification of its TPs must be addressed.

Table 2. Mean reductions of tebuconazole, cyprodinil and iprodione on peach (cv. *Spring Flame*), nectarine (cv. *Nectafun*) and apricot (cv. *Pink Cot*) after photocatalysis treatment in cold chamber for 15 d. Each value is the mean $\pm$ standard deviation of 2 replicates (5 minced fruits each) conducted on 2 separate days.

Fruit	Percentage of reduction (%)*					
	Cyprodinil		Iprodione		Tebuconazole	
	With photocatalysis unit	Without photocatalysis unit	With photocatalysis unit	Without photocatalysis unit	With photocatalysis unit	Without photocatalysis unit
Peach	33.7 $\pm$ 1.2 a	8.2 $\pm$ 1.9 b	74.3 $\pm$ 3.6 a	5.8 $\pm$ 4.7 b	3.1 $\pm$ 0.5 a	1.7 $\pm$ 0.1 b
Nectarine	30.9 $\pm$ 2.5 a	2.5 $\pm$ 0.9 b	53.7 $\pm$ 2.8 a	12.3 $\pm$ 2.9 b	5.1 $\pm$ 0.8 a	5.7 $\pm$ 0.9 a
Apricot	23.2 $\pm$ 2.7 a	5.9 $\pm$ 0.8 b	59.5 $\pm$ 2.7 a	8.8 $\pm$ 2.7 b	5.8 $\pm$ 1.0 a	5.3 $\pm$ 1.1a

*The initial concentrations of fungicides (mg kg⁻¹) in peaches, nectarines and apricots were, respectively, 20.74 $\pm$ 2.27, 12.52 $\pm$ 0.87 and 13.61 $\pm$ 1.36 for cyprodinil, 26.11 $\pm$ 1.30, 19.73 $\pm$ 2.36 and 25.94 $\pm$ 3.11 for iprodione and 7.05 $\pm$ 0.45, 6.32 $\pm$ 0.44 and 7.65 $\pm$ 1.07 for tebuconazole.

3.2. Reduction of the epiphytic microbiota of stone fruit by electrolyzed water (EW) and chlorine dioxide (ClO₂) washings and by photocatalytic treatments

The efficacy of tap water, sodium hypochlorite (SH), EW and ClO₂ washing treatments for the reduction of the epiphytic microbiota (total mesophilic aerobes and yeasts and molds) on peach, nectarine and apricot is shown in Figure 5. No significant reductions in the initial epiphytic microbiota, except in apricots, were detected after washing with tap water. SH treatment (100 mg L⁻¹ for 5 min) reduced total mesophilic aerobic (TMA) counts by 2 and 2.3 log units in peaches and apricots, respectively, and below the detection limit in nectarines. No yeasts or molds were detected after SH treatment on peaches and nectarines and 1.5 log reductions were achieved on apricots. Despite the poor results obtained by EW in the reduction of pesticide residues, its disinfectant activity on the surface of stone fruit was noticeable since neither total mesophilic aerobes nor yeasts or molds were detected on the Petri plates, obtaining more than 2 log reductions in all the stone fruits tested. The ClO₂ washing treatments (10 and

20 mg L⁻¹ for 15 min) showed that the disinfectant efficacy of ClO₂ is limited, and much lower than that observed with EW and SH treatments, with reductions that never exceeded 1.5 log units and without significant differences with an increase of the dose from 10 to 20 mg L⁻¹. Moreover, as in the case of SH, ClO₂ treatments inactivated all YAM populations on the nectarine, but a lack of decontamination efficacy of aqueous ClO₂ was detected in peach and apricot. Following an extensive review of the effectiveness of decontaminating strategies for fresh fruits and vegetables, Yoon and Lee (2017) stated that the effectiveness of the individual technologies would fluctuate variably depending on the surface properties of the fresh commodities. Investigations into the effectiveness of acidic electrolyzed water in lettuces and tomatoes (Bari et al., 2003; Koseki et al., 2001; Park et al., 2001), with a relatively smooth surface, revealed acidified electrolyzed water as being highly effective in killing or removing surface microorganisms. However, other investigations have demonstrated that cucumbers, with a rough surface, are hard to sanitize using sodium hypochlorite or chlorine dioxide (Costilow et al., 1984; Reina et al., 1995). The nectarine surface is glabrous but peach and apricot have light and dense pubescent surfaces, respectively. Fernández et al. (2011) showed that the trichomes confer a greater non-polar character to the surface and that their removal leaves the surface more polar and, therefore, more susceptible to the occurrence of interactions with water and water-soluble compounds and contaminants. Thus, the trichomes network could hinder the access of disinfectants to the microorganisms present on the surface of the fruit protecting them from the biocidal action.

The high decontaminating efficiency of electrolyzed water in the three stone fruit species stands out from the results obtained in this study. Electrolyzed water is beginning to be used as a sanitizer in the food industry since several studies have demonstrated its high antimicrobial efficacy for different types of commodities (Hao et al., 2011; Zacharia

et al., 2011; Forghani and Oh, 2013; Luo et al., 2016). Yoon and Lee (2017) reviewed and compared the effectiveness of decontaminating strategies for fresh fruits and vegetables obtaining an average $\log_{10}$ -reduction of 3.01 for EW against pathogenic and spoilage microorganisms on fresh produce, being far from the average $\log_{10}$ -reductions for sodium hypochlorite and chlorine dioxide, these being 1.12 and 1.49 respectively. These average data come mainly from studies with foodborne pathogens previously inoculated in the produce, mainly leafy vegetables, sprouts and mixed vegetables, and little data of the effect on natural micro- and microbiota has been included. The data is thus similar but only relatively comparable to ours. However, the type of produce, the type of microorganisms present, the cell type, and the location of microorganisms on the surface and in subsurface tissues all cause sanitizers to differ greatly in their ability to disinfect raw produce (Kreske et al., 2006).

Figure 5. Efficacy of tap water, sodium hypochlorite, EW and ClO₂ for the reduction of epiphytic microbiota (Total Mesophilic Aerobic and Yeast and Molds) on peach (A), nectarine (B) and apricot (C). SH 5 min: contact time of 5 min with sodium hypochlorite (100 mg L⁻¹). EW 5/15 min: contact time of 5 and 15 min with electrolyzed water. ClO₂ 10/20 mg L⁻¹ 15 min: contact time of 15 min with chlorine dioxide at 10 and 20 mg L⁻¹. Each value is the mean of 2 replicates, conducted on separate days, of 10 fruits each. Vertical bars correspond to standard deviation and different letters above the columns indicate statistical difference between the same microbial group at p < 0.05 (lowercase letter: TMA; capital letter: YAM). LOD: limit of detection. *: below the detection limit.

The reduction of the epiphytic microbiota after the storage of peaches (var. *Spring Flame*) for 15 d at 1 °C under photocatalytic conditions achieved 1.7 and 2.2 log units for

total mesophilic aerobes and yeasts and moulds, respectively (Table 3). Few authors have studied the antimicrobial effect of the photocatalytic oxidation of air during the cold storage of fruits and vegetables (Hur et al., 2005). These authors obtained a decrease of 30 % in the conidial germination of *Diaporthe actinidiae*, a fungal agent of soft rot decay in kiwifruit, when the fruit was exposed to reactive oxygen species generated by photocatalytic oxidation for 5 min. It appears that photocatalysis as a new disinfectant alternative during postharvest has not been studied in depth during the last decade. However, although few reports have been found in the literature, good results have been achieved.

Table 3. Efficacy of photocatalysis for the reduction of epiphytic microbiota (Total Mesophilic Aerobic and Yeast and Molds) on peaches cv. *Spring Flame* stored for 15 d at 1 °C and disease incidence (%) in peaches after storage for 15 d at 1 °C under photocatalysis treatment and 10 d at 22 °C. Control fruits were stored in a cold chamber without the photocatalytic unit. Each value is the mean of 2 replicates, conducted on separate days, of 10 fruits each. Different letters indicate in the same column statistical difference at $p < 0.05$.

Treatment	Total Mesophilic Aerobic (log CFU cm ²⁻¹)	Yeasts and Molds (log CFU cm ²⁻¹)	Rot incidence (%)
Control	3.6 ± 0.3a	3.4 ± 0.2a	51.1 ± 6.3a
Photocatalysis	1.9 ± 0.4b	1.2 ± 0.3b	12.6 ± 0.2b

3.3. Rot incidence in stone fruit washed with electrolyzed water (EW) or chlorine dioxide (ClO₂) solutions or stored in a photocatalytic cool chamber

The percentage of disease incidence in *Spring Flame* peaches washed with tap water, SH, EW or ClO₂ and then stored at 1 °C for 15 d followed by 10 d at 22 °C is shown in Figure 6. The incidence as number of fruits infected was 33 % in the control batch (without treatment) and all the oxidizing treatments significantly reduced this figure. The most effective were sodium hypochlorite and electrolyzed water with mean incidences

below 10 %. In contrast, ClO_2 treatments showed incidences similar to those of tap water. However, once again no differences between application times were observed, indicating that short washing periods with EW might be sufficient to disinfect the fruit surface. Future research could focus on alternatives such as EW, a technology that according to the results obtained in the current study might be a promising disinfectant for stone fruit.

Figure 6. Rot incidence (%) in peaches cv. *Spring Flame* after washing with tap water, sodium hypochlorite (SH, 100 mg L⁻¹ for 5 min), electrolyzed water (EW, 5 and 15 min) or chlorine dioxide (ClO_2 , 10 and 20 mg L⁻¹ for 15 min) and unwashed (control). Fruits were stored at 1 °C for 15 d followed by 10 d at 22 °C. Each value is the mean of 2 replicates, conducted on separate days, of 25 fruits each. Vertical bars correspond to standard deviation and different letters above the columns indicate statistical difference at $p < 0.05$.

The reduction of rot in peaches stored for 15 d at 1 °C with the photocatalysis unit followed by another 10 d at 22 °C showed promising results as the percentage of incidence was only 12.6 % (Table 3). Hence, the reduction by almost 40 % of the disease incidence in peaches suggests photocatalysis as a good disinfectant technology for stone fruit during postharvest storage prior to distribution and commercialization. Moreover, Maneerat et al. (2006) showed that photocatalysis could be an interesting disinfectant against *P.*

expansum in apple and tomato storage, significantly delaying the occurrence of the disease in the former and completely removing the infection in the latter after 1 week of storage. Future investigations based on this technology may reduce economic losses for producers caused by postharvest diseases leading to severe rot.

3.4. *Quality indices*

As it can be observed in Table 4, none of the fruits suffered significant quality changes after the application of the oxidant technologies. It can be assured that these treatments would not modify postharvest quality more than tap water washing. The data reported by Bessi et al. (2014) are consistent with our results since they showed that using EW did not affect the attributes of sweet cherries, although Hayta et al. (2015) observed some variations with different EW concentrations. Qi et al. (2018) demonstrated the capability of EW in pesticide reduction without any modification to the attributes of spinach, snap beans or grapes. Furthermore, other studies have also demonstrated that ClO₂ retains the quality of plums or apricots during the shelf life of these products (Chen et al., 2011; Zhong et al., 2006), and even reduces and delays the senescence of table grapes (Wei et al., 2018). No previous references to the application of photocatalysis to stone fruit have been found so it can be assumed that this is the first such report. In this study, the main attributes remained unchanged during cool storage for 15 d when compared with the control treatments.

611 **Table 4.** Soluble solids content (SSC), pH, titratable acidity (TA) and firmness (F) of peach (cv.
612 *Spring Flame*), nectarine (cv. *Nectafun*) and apricot (cv. *Pink Cot*) before and after washing and
613 subsequent storage at 1 °C for 15 d. Each value is the mean $\pm$ standard deviation of 25 fruits.
614 Different letters indicate in the same column statistical difference at $p < 0.05$.

	Fruit	Time	Treatment ^a	SSC (°Brix)	pH	TA (g malic acid L ⁻¹)	F (Durofel units)
615	Peach (<i>cv. Spring Flame</i>)	Before washing	-	12.3 ± 0.1 ab	3.4 ± 0.1	7.9 ± 1.4 ab	73.1 ± 4.2 ab
616		After 15 d (1 °C)	Tap water	12.1 ± 0.1 b	3.5 ± 0.0	7.8 ± 0.6 ab	73.1 ± 9.1 ab
			SH/5 min	12.2 ± 0.2 ab	3.5 ± 0.1	7.6 ± 0.5 ab	74.3 ± 8.3 ab
617			EW/25 min	12.6 ± 0.4 a	3.5 ± 0.1	8.0 ± 0.5 a	72.4 ± 2.1 b
			ClO ₂ 10/25 min	11.7 ± 0.1 c	3.6 ± 0.1	7.2 ± 0.2 b	76.6 ± 6.9 ab
			ClO ₂ 20/25 min	12.5 ± 0.2 a	3.5 ± 0.1	8.1 ± 0.5 a	78.4 ± 9.1 a
618			With photo unit	12.2 ± 0.1 ab	3.4 ± 0.1	7.5 ± 1.4 ab	76.1 ± 4.2 ab
619	Nectarine (<i>cv. Nectafun</i>)	Before washing	-	11.1 ± 0.4	3.3 ± 0.1	10.3 ± 0.4	82.2 ± 2.1 ab
		After 15 d (1 °C)	Tap water	11.2 ± 0.4	3.4 ± 0.0	10.4 ± 0.1	83.0 ± 4.8 a
			SH/5 min	11.0 ± 0.5	3.5 ± 0.0	10.3 ± 0.3	82.3 ± 5.2 ab
			EW/25 min	10.6 ± 0.7	3.4 ± 0.0	10.3 ± 1.4	80.9 ± 6.6 ab
620			ClO ₂ 10 /25 min	11.9 ± 0.1	3.4 ± 0.0	10.9 ± 0.2	77.6 ± 7.8 b
		ClO ₂ /25 min	11.7 ± 0.7	3.4 ± 0.0	11.9 ± 1.4	78.8 ± 4.7 b	
621	Apricot (<i>cv. Pink Cot</i>)	Before washing	-	14.9 ± 0.1	3.4 ± 1.2	22.9 ± 1.2 cd	33.9 ± 8.6
622		After 15 d (1 °C)	Tap water	14.6 ± 0.6	3.5 ± 0.1	21.8 ± 0.1 d	29.9 ± 8.8
			SH/5 min	15.3 ± 0.5	3.5 ± 0.1	21.6 ± 0.8 d	30.6 ± 6.5
			EW/25 min	14.9 ± 0.3	3.6 ± 0.1	23.2 ± 0.3 c	32.8 ± 12.7
			623	ClO ₂ 10/25 min	15.5 ± 0.1	3.5 ± 0.1	26.6 ± 0.2 a
			ClO ₂ 20/25 min	15.5 ± 0.3	3.6 ± 0.1	24.8 ± 0.3 b	33.9 ± 12.7

624 ^aSH/5 min (Sodium hypochlorite 100 mg L⁻¹ for 5 min), EW/25 min (electrolyzed water for 25 min), ClO₂10/25 min (chlorine dioxide 10 mg L⁻¹ for 25 min), ClO₂20/25 min (chlorine dioxide 20
 625 mg L⁻¹ for 25 min) and with photo unit (photocatalysis unit working for 15 d).

4. Conclusions

Pesticide removal from stone fruits by oxidizing technologies significantly varied with the treatment used and the target substance. EW seems to be ineffective regardless of the pesticide tested (tebuconazole, cyprodinil or iprodione) whereas ClO₂ significantly reduced tebuconazole levels and photocatalysis was active against cyprodinil and iprodione. However, electrolyzed water as a washing treatment and photocatalysis as a complementary cold storage technology have been demonstrated to have very high disinfectant activity on the surface of stone fruits and are also very effective for the control of postharvest rots. Therefore, a strategy that combines the photocatalysis treatment during cold storage in order to reduce pesticide residues and spoilage microorganisms and electrolyzed water washing in order to reduce any remaining microbial contamination, prior to commercialization, will substantially reduce disease and ensure the safety of stone fruits for human consumption.

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685 iprodione, metaldehyde, metazachlor, paraffin oil (CAS 64742-54-7), petroleum oils
686 (CAS 92062-35-6) and propargite in or on certain products.
- 687 Commission Regulation (EU) 2017/626 of 31 March 2017 amending Annexes II and III
688 to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards
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