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REVIEW

Non-thermal technologies: Solution for hazardous pesticides reduction in fruits and vegetables

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ABSTRACT
Pesticide residues in the food above the maximum permissible residual limit (MRL) for safe consumption are a severe concern today. Though unit operations employed in domestic and industrial-scale processing of foods such as high-temperature decontamination and chemical washings degrade the agrochemicals and reduce toxicity, eliminating pesticides from the fresh and raw fruits and vegetables with the retainment of nutritional and organoleptic attributes demand appropriate non-thermal technologies. In this review, the potential of novel technologies like the pulsed electric field, high-pressure processing, irradiation, ozone, ultrasonication, and cold plasma for the reduction of pesticides in fruits and vegetables have been discussed in terms of their mechanism of action, playing around factors, advantages, and limitations. All the reviewed non-thermal technologies exhibited promising effects on pesticide degradation with their unique mechanism of action. Also, these techniques' potential to reduce the pesticides below MRLs and yield nontoxic metabolites in fruits and vegetables were analyzed. However, investigating the impact of the technologies on the nutritional and organoleptic quality profile of the commodities at the processing conditions causing noticeable pesticide reduction and the pathways of degradation reactions of various pesticides with each emerging technology should be studied to enhance the applicability.

KEYWORDS
Degradation; nontoxic metabolites; non-thermal; pesticide; toxicity

Introduction

In the growing population, sustainable agricultural production is substantial to feed the world. Incessantly changing climates (Morton 2007), inexorable attack of pests and diseases (Pickett, Wadhams, and Woodcock 1997), loss of soil fertility (Chen 2006), and inability to meet the nutritional mandate of hybrid and genetically modified crops (Rengel and Damon 2008) impose the use of agrochemicals like insecticides, pesticides, herbicides, and fertilizers to increase the production of crops. Though these agrochemicals support cultivation, they exhibit harmful effects on the living species of the farming land and water (Moore 1967). Also, consuming the agricultural commodities having traces of these chemicals will cause severe health problems, which majorly involve chronic diseases like cardiovascular diseases (CVDs), various cancers, pulmonary diseases like asthma, diabetes mellitus, arthritis, reproductive and neural disorders (Mostafalou and Abdollahi 2013) in humans. This fact cannot be evaded lightly as the residual pesticide presence in the consumables specifically, in fruits and vegetables, which are often preferred to be eaten either raw or partially cooked, was encountered to a global extent.

China, the world's highest populous country, identified the residues of five toxic organophosphorus (OP) pesticides, namely dimethoate, dichlorvos, parathion, parathion-methyl, and pirimiphos-methyl, in 9% of the fruits and vegetables tested from one of the largest markets of the country (Bai, Zhou, and Wang 2006). The other South Asian nations such as Nepal (Bhandari et al. 2019), Bangladesh, Pakistan have also witnessed OP pesticide residues present in vegetables like tomato (Alamgir et al. 2013), brinjal (Iqbal et al. 2009), and fruits include apple, guava, banana, orange, grapes, and pear (Tahir et al. 2001). Market basket analysis conducted in Benin city having the largest fruit vegetable markets of western Africa, found the occurrence of organochlorine pesticides, particularly gamma lindane in watermelon, cucumber, and onions (Atuanya and Onuoha 2018). Not only the market vegetables but also the tomato samples procured from the farm fields of Tanzania, an eastern African country, were detected with a very high level of pesticides such as permethrin (5.3 ppm/day), chlorpyrifos (7.5 ppm/day), and ridomil (2.9 ppm/day) (Kariathi, Kassim, and Kimanya 2016). Market survey on detection of chemicals includes fungicides, insecticides like neonicotinoids and pyrethroids, and herbicides in green leafy vegetables conducted in Italy disclosed the pesticide contamination of around 53.33% of vegetables tested, among which 59% were precut vegetables, and 41% were uncut vegetables (Santarelli et al. 2018). In Poland, 19 different fruits and vegetables were assessed for organophosphorus pesticides in the peel and in each sample's pulp to evaluate whether the level of pesticides was

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under control (Witczak et al. 2018). The present study identified that the presence of chlorpyrifos was exceeding in all the fruits and vegetable peels, i.e., in the range of 9.3 mg/kg and 31 mg/kg respectively among the investigated organophosphorus pesticides such as ethoprophos, diazinon, chlorpyrifos-methyl, parathion-methyl, fenchlorphos, chlorpyrifos, and merfos. Explicitly, the peel of potatoes and pulp of zucchini was detected with a higher level of parathion-methyl. Though many investigations deal with pesticide residues in all agricultural commodities classes, these studies majorly emphasize the recent pesticide outbreaks in fruits and vegetables in various countries.

There can be two ways of managing pesticide levels and their residues in food, either by elimination or by degradation through various mechanisms. The customary unit operations involved in primary and secondary foods' processing were determined to influence the pesticide levels innately. The first and foremost unit operation is necessarily being done in every processing line, i.e., 'washing' reduces the pesticide levels to a certain extent, however, depending on the hydrophilicity of pesticides. Several auxiliary factors include water temperature, pH, and secondary oxidants, which were manipulated to enhance the reduction efficiency.

A study on washing pretreatment for pesticide reduction in tomatoes showed the potential of acetic acid (of 10% concentration) washing to lessen the level of pesticides by 33.7% to 93.7%, followed by 10% sodium chloride washing giving a reduction percentage of about 27.2% to 91.4% which varied according to the nature of pesticides (Abou-Arab 1999). Another study on home processing of okra, cauliflower, and brinjal also explored the maximum of 74% pesticide reduction with 1 min washing in tap water (Kumari 2008). Despite these investigations, the solubility of the pesticides in water plays a significant role in eliminating or dissolving adhered pesticides. The above studies also explored the removal of pesticides present in the exocarp of the fruits and vegetables by peeling or juicing. Though pesticide application to the crop may begin from the initial stages of plant growth, it predominates when the fruit or vegetable starts to appear. Studies on the effect of peeling on residual pesticide reduction in carrots explained the effective removal of pesticides adhering to peel and crown of carrots, transmitted from the soil surface to the product tissues (Burchat et al. 1998). The heat processing methods like saucing, canning, blanching, and boiling were found to significantly reduce the pesticide levels as they cause pyrolysis of the pesticides. Investigations on the effect of boiling, steaming, and combined treatments revealed that boiling the commodity with chemicals like zinc chloride, potassium metabisulphite and sodium bicarbonate for 3 min indulge in the maximum of 81% reduction despite the characteristics of pesticides (Hanafi, Elsheshetawy, and Faied 2016). However, boiling more than 5 min found to exert the loss of organoleptic properties of the vegetables. The processing of vegetables through canning was also observed to influence the pesticide residues but only about 50% (Chavarri, Herrera, and Arino 2005). About 61% of pesticide, the reduction was found after three months of storage of canned food. However, even after two years of storage, there was still an 11% residual presence in the canned food, which depicts that storage had no impact on pesticide reduction and further demands an efficient pesticide reduction process. Though the research on home processing of fruits and vegetables describes better results on pesticide reduction, they implore a dependency on characteristics of pesticides like surface adherence, hydrophilicity and, thermal stability. Also, the high temperature involved processes reduce nutritional and taste-related attributes.

To overcome the drawbacks of these conventional methods and to facilitate pesticide reduction in fresh fruits and vegetable products, non-thermal technologies were introduced. In the existing review, the potential of the emerging technologies like pulsed electric field processing, gamma irradiation, ozonation, ultrasonication, high-pressure processing, and cold plasma for pesticide reduction in fruits and vegetables were delineated. The mechanism of action involved in each non-thermal method and its advantages and limitations were given in Table 1. The other factors affecting the pesticide reduction (as given in Figure 1), such as the pesticide characteristics to be dissipated and the food commodity, were discussed in relation to each non-thermal technology's process parameters. Though there are available reviews (Bhilwadikar et al. 2019) discussing the potential of non-thermal technologies on pesticide reduction, the current review exclusively compares and evaluate the efficacy of non-thermal technologies to reduce the pesticides to maximum permissible limits (MRLs) as prescribed by regulatory bodies along with the toxicity of the metabolites produced in view of the consumer safety. In addition, the recent significant pesticide dissipation studies on fruits and vegetables were also discussed.

Pulsed electric field (PEF)

Pulsed electric field processing involves the application of intense electric pulses of electric field strength 10–80 kV/cm for a short duration of time (μs). There are two different hypothesized mechanisms of pesticide reduction by PEF. According to Chen et al. (2009) intense electric pulses make the polar molecules to rotate and vibrate dynamically, which facilitates the degradation of neighboring pesticide compounds. The study had also reported a maximum percentage reduction of methamidophos and chlorpyrifos in apple juice with the electric field strength of 20 kV/cm at the maximum pulse number. Zhang et al. (2012a) also studied the influence of PEF on dimethoate and diazinon in apple juice to cause a maximum of 47.6% and 34.7% reduction respectively at 20 kV/cm with 260 μs treatment time and stated that hydroxyl radicals generated on the application of PEF react with the pesticide compounds and degrade it.

The process variables such as electric field strength, treatment time, and pulse number significantly influence the process's degradation efficiency. The higher the electric field strength, the higher the pesticide degradation due to the production of more reactive species and radicals. However, pulse number also influences the degradation efficiency.

Table 1. Mechanism of action, advantages, and limitation of non-thermal methods.

Sl. No	Method	Mechanism of action	Advantages	Limitations
1.	Gamma radiation	Oxidation through radicals and reactive species; Reaction with the ionizing radiation.	Commercially available technique for bulk quantity of samples;	Rough-surfaced foods will not be effectively reduced for pesticides; Lesser feasibility; Need to concentrate on packaging material used; Care to be taken for labor safety;
2.	Ozone (O_3)	Oxidation through radicals and reactive species	Relatively cheaper and feasible to operate; Free of residues and pollutants on disposal; Higher percentage of reduction;	Higher treatment time required; Temperature-dependent reduction occurs; Higher risk of oxidative degradation of bio actives in the commodity;
3.	Pulsed Electric Field	Rotation/ vibration of polar molecules & oxidation via the hydroxyl radicals	Very less treatment time required; No significant changes in the product quality;	Higher capital cost; Generally, liquid foods can be processed; Need for conducting and inert medium to treat solid foods;
4.	High-pressure processing	Weakening the hydrophobic interactions between the pesticides and water molecules in the food	Commercially available technique for bulk quantity of samples; Biochemical and sensory characteristics of the commodity is retained; Can be used along with the microbial degradation & enzyme inactivation purpose;	Under-explored for pesticide reduction; Loss of structural integrity of food above 75 MPa;
5.	Ultrasound	Localized temperature formation causes pyrolysis of pesticides; Free radicals and reactive species produced on cavitation react with the pesticides.	Commercially available technique even for domestic application; Applicable for solid as well liquid foods; Can be used along as a pretreatment for extraction and drying as it helps enhancing mass transfer.	Give better reduction when applied in combination with other treatments; Relatively higher nutritional and structural losses to the commodity.
6.	Cold plasma	Oxidative reactions with the free radicals and reactive species;	Higher Percentage of reduction; Surface reactions promise retainment of product freshness and physico chemical characteristics.	Studies on scaling up the technology is needed; The penetration depth of plasma is lesser, which thereby produces inconsistent reduction efficiency;

More the number of electric pulses per unit time, the vibration of molecules would be more instant; thus, the degradation would be prompted. Also, at a longer treatment time, the degradation reaction would be prolonged, resulting in a higher percentage of pesticide reduction. Delsart et al. (2016) investigated the effect of PEF with the electric field strength of 5–20 kV/cm for 0.5–2 ms in order to reduce the pesticides like Pyrimethanil, Vinclozolin, Cyprodinil, Procymidone in white wine and a higher percentage of reduction ranging from 25% to 49% at 20 kV/cm with 2 ms was observed. At the same time, no significant changes in the pesticide degradation percentage with an increase in treatment time were observed by Zhang et al. (2012a). The reason behind this would be variations exhibited by the pesticides in their chemical characteristics.

The process variables and the chemical structure and properties of the pesticides present will also influence the reduction of efficiency and degradation kinetics. The major constraint of PEF is that the efficacy of the treatment depends on the conductivity of the material to be treated (Ricci et al. 2018). This restricts the application of PEF to solid food matrices like whole fruits and vegetables. However, a conducting and non-reacting liquid medium can be used to treat the whole fruits and vegetables. Nevertheless, the above studies have not explored the impact of PEF on the quality attributes of the treated commodity, which is necessary to be considered for the optimization of process parameters to give a higher percentage of pesticide reduction without causing much loss in the physicochemical and sensory attributes of the commodity. Recently, a study conducted on sour cherries experimented with the efficacy of pulsed electric field in combinations with ozone and ultrasound processing to degrade some of the pesticides like chlorpyrifos ethyl, t-fluvalinate, cyprodinil, pyraclostrobin, and malathion along with the changes in the physicochemical, sensory, bioactive and microbial stability of the commodity explicitly pertaining to the pathogens like *Escherichia coli* O157: H7, *Bacillus cereus*, *Pseudomonas syringae*, and *Penicillum expansum* (Akdemir Evrendilek, Keskin, and Golge 2020). The authors tried to optimize the best

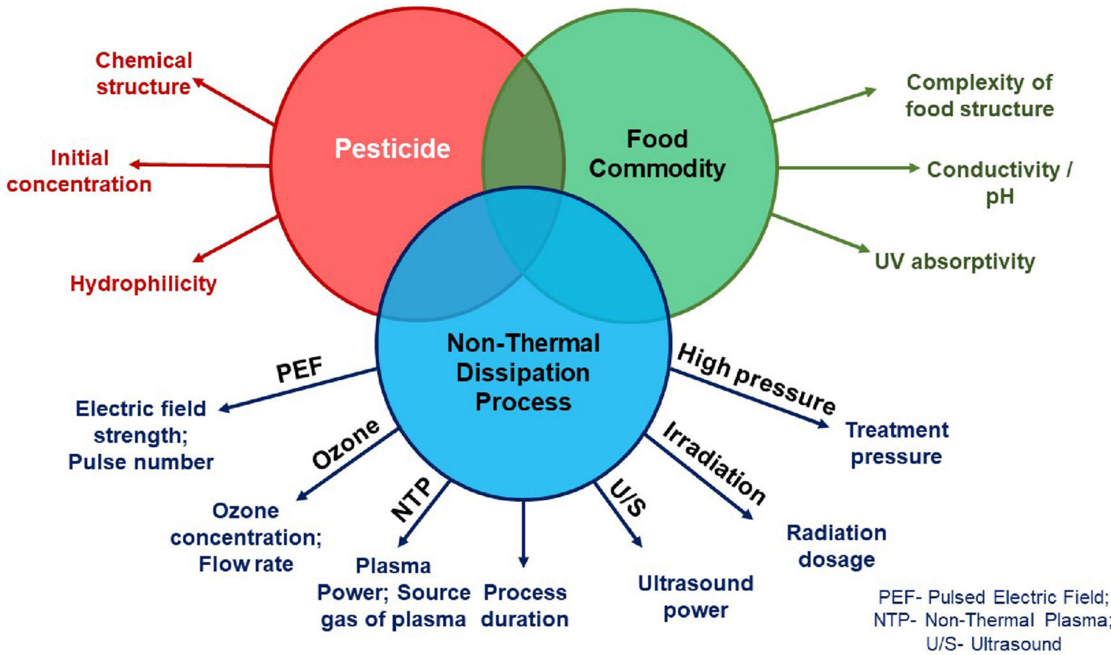

Figure 1. Factors affecting the pesticide dissipation efficacy.

treatment conditions to obtain significant pesticides and microbial reduction with non-significant changes in the physicochemical, sensory, and bioactive attributes and concluded that the combination of pulsed electric field treatment at 24.7 kV/cm for 655 µs treatment time with 3 min ozone treatment of concentration 20.2 g/m^3 and 35 kHz of ultrasound for 3 min was giving the best pesticide and microbial reduction. However, considering the physicochemical, sensory, and bioactive attributes along, pulsed electric field treatment outstand the other treatments by providing better stability of the former. The study proves that when the combinations of non-thermal technologies are used, the commodity's chemical and microbial safety is assured due to their synergistic working mechanism with lesser treatment time. However, when multiple technologies are involved, the operation cost would increase, and the feasibility may become uncertain. Also, pulsed electric field treatment's ability to preserve the freshness related attributes of the fruit despite pesticide degradation and microbial inactivation proves it to be a promising non-thermal technology.

Irradiation

Subjecting or exposing the food to ionizing electromagnetic radiations such as gamma rays, x-rays, and electron beams is known as irradiation. Gamma rays are the widely used ionizing radiations of highest energy (>100 keV) in food as their penetrating depth is relatively higher compared to the other ionizing radiations (Hayashi 1991). Gamma irradiation of food produces free radicals and reactive species, which tend to react with the pesticide molecules to stabilize, thus causing the pesticide's degradation. However, gamma irradiation of fruits and vegetables was underexplored for pesticide reduction.

The available study on gamma irradiation of potatoes to reduce aldrin, endrin, and heptachlor epoxide (Solar, Liuzzo, and Novak 1971) exhibits a maximum of 42.21% reduction of heptachlor epoxide among all the studied pesticides at the extreme process conditions of 8.7 kGy irradiation for 1 h. Basfar, Mohamed, and Al-Saqer (2012) also studied gamma irradiation's effect on reducing pesticides like malathion, pirimiphos-methyl, and cypermethrin as aqueous suspensions and as inoculated in potatoes, onions, grapes, and dates. In the present study, the pesticides and their initial target concentrations were selected based on the encountered incidences on the presence of pesticide residues in fruits and vegetables. The study showed a comparatively insignificant pesticide reduction percentage in the selected vegetables and fruits even with 7 kGy irradiation for 29 min, while irradiation of pesticides as aqueous suspensions exposed a considerable percentage of reduction. The previously mentioned study reveals that the reduction efficiency is greatly influenced by the concentration and type of pesticide and its interaction with the commodity. To give an instant, dates spiked with 8 ppm of malathion had been observed with no effect on pesticide reduction when irradiating with 1 kGy dosage for 29 min whereas, in dates of 0.1 ppm spiked pirimiphos-methyl was reduced by 44.44% with the same process conditions. Nonetheless, at the same 1 kGy dosage for 29 min, potatoes spiked with 0.05 ppm of pirimiphos-methyl were observed with an 18% reduction in the pesticide, which in turn explicates the effect of structural attributes of fruits and vegetable to cause noticeable pesticide reduction.

The significance of complex food structure hindering free radicals' activity over the toxic pesticides was clearly shown by Chowdhury et al. (2014) in the study on the effect of gamma irradiation of the cut vegetables like tomatoes, capsicum, and cucumbers. In all the tested vegetables, with gamma irradiation of 1 kGy, a maximum of 95% reduction of diazinon, chlorpyrifos, and phosphamidon was attained. As the surface area of the cut vegetables is higher than that of the whole vegetables, reduction efficiency would be higher. Though gamma irradiation promises better reduction percentages of pesticides, the feasibility of operation and consumer acceptance of irradiated food is indecisive. Also, the packaging material used in the commodities for in package irradiation should be given superior consideration as the polymer's radical-induced reactions could instigate toxic interactions with the food .

Ozone

Ozone is the highly reactive and unstable form of oxygen produced on the application of high energy to the oxygen molecule (O_2), causing the disassociation of a molecule into two oxygen atoms ($O^{\cdot} + O^{\cdot}$) followed by association of an atom with an oxygen molecule to give an ozone molecule (O_3). Ozone found its application in many food processing treatments for microbial decontamination and disinfestation because of its highly reactive and oxidative nature. Similarly, both in its gaseous form and in its dissolved form, ozone was investigated for better pesticide reduction efficacies due to its high oxidation potential. Ozonated water washing was feasible and a useful technique for pesticide degradation in aqueous suspensions and fruits and vegetables (Chen, Lin, and Kuo 2013; Wu et al. 2007). Al-Dabbas et al. (2018) observed 98% and 87% reduction in chlorpyrifos and cypermethrin in tomato fruits by ozonated water washing with 0.4 ppm ozone for 30 min. The ozone molecules being extremely unstable will react with the pesticide compounds to degrade them into simpler forms, which in turn reduce the concentration of the toxic parent pesticide compound (Lozowicka et al. 2016). Since the number of pesticide molecules reduced depends on the number of ozone molecules available for the degradation reaction, the process parameters like concentration of ozone and its flow rate significantly affect the degradation percentage.

Effect of ozone micro bubbling on fenitrothion and benomyl residues in red and green persimmon leaves were compared (Ikeura et al. 2013). The microbubbles inside water generate hydroxyl radicals, which give rise to a synergistic effect along with ozone and thereby increase the reduction to 75% with 2.0 ppm ozone for 15 min. But according to Sadło et al. (2017), gaseous ozone was giving a higher percentage of pesticide reduction (captan, boscalid, and pyraclostrobin) in apples compared to ozonated water washing, which might be due to the higher stability of ozone in its gaseous form than its dissolved form. However, compared with simple tap water washing, ozonated water washing was found to give prominent pesticide reduction percentage as observed by Souza et al. (2018) in the case of difenoconazole (98%) and linuron (95%) reduction in carrots with 10 ppm of ozone for 120 min exposure. Rodrigues et al. (2019) also studied the effect of saturated ozone water washing and continuous ozone bubbling compared with the conventional detergent washing to reduce the fungicides like azoxystrobin, chlorothalonil, and difenoconazole in tomatoes. Ozone treatment predominated the conventional detergent washing in terms of both pesticide dissipation efficiency as well as the retention of physicochemical attributes of tomatoes during the storage of 13 days at 23 ± 1 °C. Furthermore, continuous ozone bubbling of 3 ppm with the flow rate of 2 L/min was found to be giving higher pesticide reduction of 70–90% than the saturated ozone water washing for the same treatment time of 30 min. The reason would be the unceasing production of ozone in continuous bubbling, thereby enhancing the oxidation of pesticides.

Unlike the above studies, Karaca and Karaca (2019) investigated the effect of atmospheric ozone storage on the reduction of several pesticides in table grapes. The author observed a maximum of 3.6-fold reduction in all the pesticides after 36 days of storage at 0.3 µL/L ozone concentration inside the cold storage of 2 °C and 95% RH. In a similar study on enriched ozone storage for dissipation of pesticides like azoxystrobin, bupirimate, carbendazim, penconazole, trifloxystrobin, and triadimenol in table grapes, Tabakoglu and Karaca (2018) explored the physicochemical attributes of grapes after the ozone storage and concluded that there were no significant differences in the physicochemical properties like brix, pH, weight loss and total acidity of grapes stored in ozone atmosphere in comparison with the grapes stored under ambient conditions. Besides, the studied pesticides exhibited varying resistance to dissipation in terms of the time taken for their reduction. Among all, azoxystrobin was found to be more susceptible to oxidation, while trifloxystrobin was more resistant. However, in the study by Rodrigues et al. (2019), azoxystrobin was relatively more stable than difenoconazole and chlorothalonil. This could be due to their differing chemical structures. In a review of non-thermal pesticide dissipation technologies, Misra (2015) explained all the intrinsic and extrinsic factors affecting the pesticide dissipation efficiency of ozone processing. Also, Pandiselvam et al. (2020). Wang, Wang, et al. (2019) exclusively reviewed the potential of ozone processing on all the food commodities' pesticide residues. Though ozonation is giving promising pesticide reduction effects, the time taken for obtaining noticeable results is relatively higher. Also, the query on diminished efficacy due to superficial reaction is still indecisive.

Ultrasonication

Subjecting the food system to high-frequency sonic waves of >20 kHz results in rapid formation and disruption of bubbles called cavitation. Cavitation owes to the generation of free radicals, localized hot and high-pressure spots, and cell disruption (Feng, Barbosa-Cánovas, and Weiss 2011). This phenomenon facilitates pyrolysis and oxidation of the toxic agrochemicals. Also, the disrupted cells bring on more contact area for the diffusion of oxidants causing useful reduction reactions. Hence, ultrasonication was widely preferred for enhancing the efficacy over other treatments like ozone, UV radiation, and low-intensity electrical current.

Fan et al. (2015) found a maximum reduction of 80% in methamidophos and dichlorvos from lettuce by 75 mg/L of ozone bubbled along with 1000 W powered ultrasonic bath having 25 kHz frequency. Similarly, Cengiz et al. (2018) stated a maximum percentage of reduction in captan (94.26%), metalaxyl (79.78%), thiamethoxam (92.58%) at 1400 mA electrical current with 40 kHz ultrasonic bath after 10 min treatment in tomatoes. However, ultrasonic washing was also solely investigated for pesticide degradation in Yue et al. (2009). Zhou et al. (2019) studied the influence of sole ultrasonic washing on the dissipation of difenoconazole, azoxystrobin, thiamethoxam, abamectin B1a and B1b, and tebuconazole in rape and grapes using the commercial ultrasonic dishwasher. The author compared the efficiency of ultrasound washing with tap water washing and inferred that ultrasound washing treatment gave an exceptionally higher percentage of reduction in both rape and grape samples. However, there were variations in the reduction percentage with the varying pesticides. Also, comparing rape and grape, the grape was observed with higher reductions in pesticides due to its increased surface area. Correspondingly the surface morphology of the commodity facilitates adhesion and adsorption of the pesticides. So, it is clear from the above study that dissipation efficiency depends on the commodity's surface characteristics. Thus to scale up the technology for commercial application, process parameters should be determined after studying the efficacy for a particular required commodity. Zhu et al. (2019) have studied the effect of ultrasonic washing on the degradation of chlorothalonil, pyrazophos, and carbendazim residues form pakchoi (Chinese cabbage). The author observed an increase in pesticide reduction with increasing ultrasonic power and decreasing ultrasound frequency. Nevertheless, as an undesirable outcome, the vitamin C content and physical structure of pakchoi decreased with process parameters required for higher pesticide reduction. This necessitates more research on optimization of treatment conditions considering the macro and micronutrients stability as well. However, in another study on ultrasonic degradation of phorate in apple juice, the chemical composition particularly the sucrose, glucose, and fructose content of the apple juice, was observed to be significantly unchanged even at the extreme operating conditions of 500 W ultrasonic power for 120 min (Zhang et al. 2012b). This suggests that the impact on the nutritional properties would be varying for commodities.

Yet, ultrasonication is an under-explored area for the pesticide dissipation objective; the sonochemical and sonothermal effects tend to cause degradation reactions in the pesticides while the sono-physical effect will magnify the degradation efficiency through synergistic effects. Azam et al. (2020) exclusively explained the various systems available and the efficiency of ultrasound treatment in their process parameters to cause pesticide degradation and its other applications.

High-pressure processing (HPP)

High-pressure processing of foods involves the application of extreme pressure ranging from 100–800 MPa (Cheftel 1995) in an intact vessel through a transmitting fluid. When the food system is subjected to intense pressure, the hydrogen bonds between the molecular compounds will be affected significantly. This weakens the hydrophobic interactions between the water-insoluble pesticide carbon chains and the polar molecules of the food. Consequently, the hydrogen atoms in the water molecules open vacancies for the pesticide compounds to form innocuous degraded pesticide metabolites leading to its depletion. In HPP, pressuring the food above 200 MPa causes critical damages in its structure, thereby increasing pesticide penetration inside the fruit through ruptured exocarp. This, in turn, reduces the percentage of pesticide reduction above the critical pressure level.

Iizuka, Maeda, and Shimizu (2013) discovered a maximum of 76% reduction in chlorpyrifos on cherry tomatoes at 30 min pressurizing with 75 MPa, above which a reduction in pesticide degradation occurs as discussed above. Nonetheless, at this pressure level, the texture of the fruits was significantly affected. Since HPP causes a major impact on the textural attributes of fruits, further studies are substantial to facilitate the HPP application for pesticide reduction in whole fruits and vegetables. However, there was no literature on pesticide reduction in liquid foods with high-pressure processing.

Cold plasma

Plasma is known as the fourth state of matter produced on energizing the gaseous molecules. It is a mixture of high-velocity electrons, ionized atoms and molecules, free radicals, atoms in their ground and excited state, and UV radiations (Ratish Ramanan, Sarumathi, and Mahendran 2018). Plasmas are categorized into thermal and non-thermal plasma depends on the thermal equilibrium between the electrons and the gas molecules. When the electrons are in a thermal non-equilibrium, non-thermal, or cold plasma is produced (Mahendran, Abirami, and Alagusundaram 2017). Non-thermal cold plasma was explored for a wide range of food applications, among which pesticide reduction potential on agricultural commodities was the recently investigated application of interest (Phan et al. 2017). The generated reactive species, free radicals, excited atoms, and molecules of plasma were believed to cause oxidative interactions with the pesticides without causing significant changes in their principal components (Misra et al. 2014).

The plasma species supplant the phosphoryl groups of pesticides in organophosphorus pesticide and form phosphoxons, which are primary toxic, unstable metabolites of the parent pesticides. Since this reaction is specific for organophosphorus pesticides, the toxicity of the produced metabolites varies according to the chemical structure and identities of the pesticides. In addition to the reactive oxygen species, the energized nitrogen compounds, i.e., reactive nitrogen species, were also involved in nitration and nitrosation of phenolic groups in pesticides to yield innocuous products with water as an adduct (Magureanu, Bradu, and Parvulescu 2018). However, plasma species' propagative reactions until termination lean toward the mineralization of pesticides into simple organic compounds and carbon-dioxide (Hu et al. 2013). There are different reactions between the plasma species and the pesticide compounds as per their changes in structural and chemical attributes.

There are many factors like electrodes distance, type of gas used in plasma and its flow rate, plasma power or voltage, treatment, or the exposure time, influencing the effectiveness of plasma for pesticide reduction. However, all the above process parameters lead to the plasma mixture's attributes, i.e., the amount of active species available for the pesticide reaction to being degraded. Misra et al. (2014) observed the highest percentage of reduction in the pesticides azoxystrobin (69%), cyprodinil (45%), fludioxonil (71%), pyriproxyfen (46%) in strawberry at 80 kV dielectric barrier discharge plasma (DBD) exposures for 5 min which was the maximum operating conditions. Similar results were obtained by Sarangapani et al. (2017) in the case of boscalid (75%) and imidacloprid (80%) degradation in blueberries. Dorraki et al. (2016) also acquired comparable outcomes for 88% diazinon degradation in cucumber with 0.75 W plasma power for 15 min treatment. Similarly, in the study on reducing chlorpyrifos content from tomato, a maximum of 89.18% reduction has been obtained with the power of 5 W treated for 6 min (Ranjitha Gracy, Gupta, and Mahendran 2019b). The authors have also screened the presence of a nontoxic secondary metabolite 3, 5, 6- Trichloropyridinol after the plasma treatment. This metabolite of chlorpyrifos degradation was relatively innocuous than the parent chlorpyrifos and its primary metabolite chlorpyrifos-oxon (Hanley, Carney, and Johnson 2000). Despite the promising percentage of reduction, the authors have encountered statistically significant changes in the texture, carotenoid, and phenolic contents of the fruit, which are slightly undesirable. However, there have been no visible modifications. In the same way, a study investigating the effect of gas-phase surface barrier discharge plasma (Zhou et al. 2018) to reduce the organo-phosphorus pesticides like omethoate (99.55%) and dichlorvos (96.83%) in goji berry explained the complete degradation of studied pesticides into innocuous products of PO_4^{3-}, SO_4^{2-} and Cl^- after the 10 kV plasma treatment for 30 min. This, in turn, explains the cold plasma process's superiority by reducing the parent molecule and reducing metabolites' toxicity.

The existing studies on plasma degradation of pesticides, higher power levels, gas flow rate, and treatment time eventually result in a higher percentage of pesticide concentration reduction. Even though in some studies, intermediate flow rates were observed to give the maximum percentage of reduction in the pesticide levels above which there occurs a decline in the reduction efficiency as observed by Phan et al. (2018) in the gliding arc plasma decontamination of chlorpyrifos and cypermethrin in mangoes with the varying flow rate (2–8 L/min) of plasma power 600 W treated for 5–10 min. The author stated that at 5 L/min flow rate, plasma treatment for 5 min was given a noticeable reduction of 74% and 62.9% for chlorpyrifos and cypermethrin. It was also reported that, at higher flow rates (> 5 L/min), there would not be sufficient contact between the water molecules and the gliding arc as water flows faster, which in turn reduces the concentration of free radicals generated. The study mentioned above has also observed some significant changes in the physicochemical characteristics such as the total phenolic content, carotenoids, and titrable acidity of the commodity due to the interaction of oxidative species as discussed in Ranjitha Gracy, Gupta, and Mahendran (2019b).

Zheng et al. (2019) demonstrated Plasma Activated Water (PAW)'s efficiency to degrade phoxim on table grapes. Plasma activated water is produced when a plasma reactor actuates in the proximity of water molecules by direct (in-situ) or indirect (ex-situ) ionization resulting in the generation of immense hydroxyl radicals and acidic nitrogen species dissolved in it (Kamgang-Youbi et al. 2009). Since in PAW, the plasma species are in a dissolved form, which facilitates faster stabilization of radicals, ROS and RNS, the degradation time would be relatively prolonged as compared with the gaseous plasma process. This fact was proven by Zheng et al. (2019) findings as 30 min of PAW preparation time with 10 min of treatment time was required to obtain a 73.60% reduction in phoxim concentration with 5 L/min PAW. The author observed no significant changes in the primary physicochemical characteristics, i.e., the color, texture, sugar content, and vitamin C content of grapes, which promises the supremacy of the process to reduce the pesticides and the quality retention. Sawangrat et al. (2019) also studied the impact of 60 min treatment of PAW produced with the plasma power of 125 W and a flow rate of 15 L/min on the reduction of cypermethrin in tangerine fruits. Results summarized a reduction in the pesticide concentration from 1 ppm to 0.25 ppm after the PAW treatment and the sensory attributes of the tangerine fruits such as the appearance, smell, acidic flavor, and sweetness retained compared with the control fruits. Likewise, the study on the efficacy of ex-situ PAW treatment to reduce the chlorpyrifos content in tomatoes resulted in a maximum of 52% reduction with 200 V plasma operating voltage and a 10 L/h flow rate when treated for 15 min (experimental PAW set-up used was given in Figure 2) (Ranjitha Gracy, Gupta, and Mahendran 2019a).

It was found from the above studies that the PAW preparation time or the treatment time is the deciding factor of pesticide reduction in addition to the flow rate. However, comparing with the direct (DBD, surface barrier discharge) or semi-direct plasma processes (Gliding arc discharge), PAW requires longer treatment time for a higher percentage of pesticide dissipation. As the reactive species are susceptible to the type of plasma and the process parameters, playing around these factors results in optimizing treatment conditions for better reduction efficiency. Some existing studies of the above mentioned non-thermal techniques for pesticide reduction in fruits and vegetables were briefly elucidated in Table 2.

Comparative evaluation of non-thermal techniques for pesticide dissipation efficacy

The efficacy of non-thermal processing (NTP) techniques are conclusively compared and presented in Table 3, which

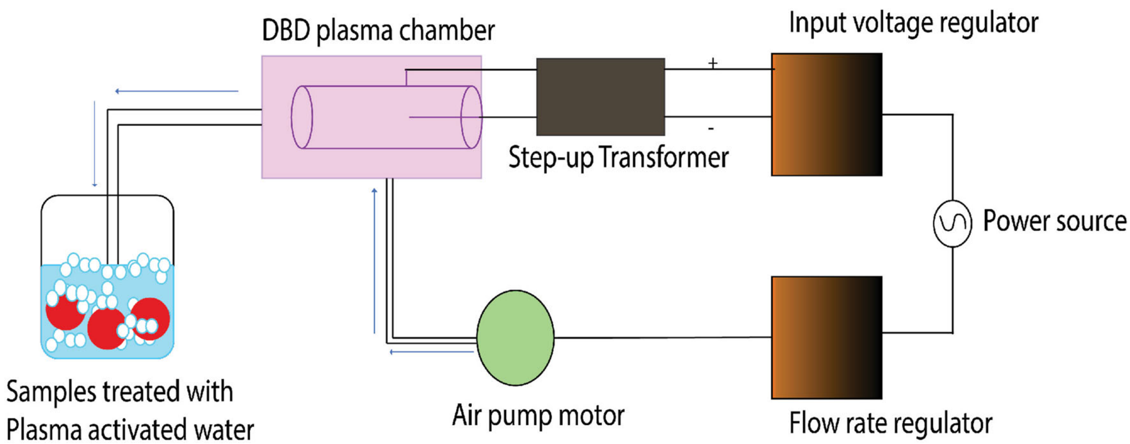

Figure 2. Experimental PAW set-up used for chlorpyrifos dissipation in tomatoes.

contains the summary of percentage reduction of various studied pesticides in fruits and vegetables along with their Maximum Residual Limits (MRLs) as stated by the European Food Safety Authority (EFSA) and Codex Alimentarius (CODEX) commission. In case more than a single study has been done on the same pesticide with the same NTP technique, the highest percentage of reduction obtained among the studies was considered as the representative percentage of reduction, signifying the potential of the technique. Alike, there would be varying MRL values available for different food commodities as per the diverse national and international regulatory bodies. However, the lowest of all of the fruits and vegetables legislated by the widely enforced regulatory bodies such as EFSA and CODEX was tabulated, taking the safety and broad applicability into account. Also, the studied pesticide's highest concentration (exceeding the MRL) encountered in the commercially available samples from markets and farms as per the literature in the last decade were included disregarding their geographical locations, type, and variety of fruits and vegetables in order to identify the scope as well as the potential of the discussed NTP techniques.

Almost all the pesticides studied by the NTP technologies were reported for concentrations exceeding the MRLs in fruits and vegetables of markets and farms from varying localities throughout the world in Asian (China, Nepal, South Korea, Thailand, Pakistan, Egypt, Jordan, Kazakhstan), European (Italy, Poland, Denmark), African (Algeria, Ghana, Nigeria), and South American (Chile, Argentina) countries with the prevalence in the Asian and African countries. Among the 35 pesticides tabulated, 15 pesticides (Diazinon, Pyrimethanil, Vinclozolin, Γ- fluvalinate, Aldrin, Endrin, Heptachlor, Pirimiphos-methyl, Fenitrothion, Benomyl, Captan, Trifloxystrobin, Thiamethoxam, Phorate, Paraoxon) which are mostly but not exclusively banned and restricted for use. The higher toxicity of these pesticides in many countries was reported with concentration below 1 ppm though that exceeds the MRL value. This thereby stands as a threat to the safety of the consumers. However, on the application of NTP technologies such as Pulsed Electric Field (PEF), Ozone (O_3), Gamma irradiation, and Cold Plasma, these pesticides were observed to be reduced below or nearer to the MRL levels. O_3 processing was especially studied mainly because of its relatively higher feasible and cost-effective nature, with a promising pesticide reduction range of 38–98%. Though the cold plasma technique is in its early establishment stage with a few studies for pesticide dissipation, the technique's potential is definite as the percentage of pesticide reduction ranges from 52–98%. Besides, the different types of plasma reactor used such as Dielectric Barrier Discharge Plasma (DBD), Gliding Arc Discharge (GAP), and Plasma Activated Water (PAW) were giving varying efficacies with the predominance of DBD, which might be attributed to its impact over continuous as well as larger production of oxidative species and free radicals. Similarly, Gamma irradiation was also found to cause pesticide reduction of 4–100% with high treatment capacity and penetration power in spite of its demands on labor safety and product packaging requirements. The minimum pesticide reduction to the least of 4% is due to the higher structural stability of the treated pesticide. PEF stands as the non-thermal technology of relatively lesser efficacy with the pesticide reduction range of 25–76% for varying pesticides, however, with the very less treatment time of about microseconds. Nevertheless, PEF, when applied along with the other NTP techniques like O_3 processing and ultrasonication, would increase the percentage of reduction by two-fold as in the case of cyprodinil and pyraclostrobin (Akdemir Evrendilek, Keskin, and Golge 2020) (from Table 3). Comparing the potential of all the non-thermal techniques for the reduction of the same pesticide compound, for example, in the case of chlorpyrifos reduction, PAW treatment was giving the least percentage of reduction followed by GAP, High-Pressure Processing (HPP), PEF, DBD, Gamma and O_3. Comparing different techniques applied to different fruits and vegetables with varying process parameters would be inappropriate to analyze the efficacy of the technologies; this would provide a generalized conception about the relative potential of the technologies.

Unlike the other non-thermal technologies, HPP and Ultrasonication (U/S) were not studied extensively for a number of pesticides. Yet, their incurred percentage of reduction for chlorpyrifos, difenoconazole, azoxystrobin, and chlorothalonil were significant. In spite of commercial availability, the lesser interest in these non-thermal technologies for pesticide reduction in whole fruits and vegetables would be due to the modifications in the textural attributes of the

Table 2. Existing non-thermal pesticide reduction studies on fruits and vegetables.

Method	Pesticide	Sample	Process parameters	Key findings	Reference
Gamma irradiation	Aldrin, Heptachlor epoxide, Endrin.	Potato.	Cobalt-60 gamma source; 8.7 kGy; 1-hour irradiation.	The maximum percentage of reduction: Aldrin – 30.28%, Heptachlor epoxide – 42.21%, Endrin – 4.20%.	(Solar, Liuzzo, and Novak 1971)
	Malathion, Pirimiphos-methyl, Cypermethrin.	Potato, onion, grapes, dates.	Cobalt-60 gamma source; Dosage of 0.15–7 kGy; Irradiation time 0.4–29 minutes.	Potato – pirimiphos methyl – 18% at 1 kGy; Onion – no reduction in any pesticides; Grapes – Malathion – 4% at 7 kGy; Pirimiphos methyl – 6% at 2 kGy, 19% at 7 kGy; Cypermethrin – 3% at 7 kGy. Dates – Pirimiphos-methyl – 44% at 7 kGy.	(Basfar, Mohamed, and Al-Saqer 2012)
	Diazinon, Phosphamidon, Chlorpyrifos.	Packed minimally processed cucumber, tomato, and capsicum.	Cobalt-60 gamma source; 0.5 & 1 kGy.	Capsicum – Diazinon- 85–90%, Phosphamidon – 80–91%, Cucumber – Chlorpyrifos 90–95%,	(Chowdhury et al. 2014)
Ozone (O_3) bubbling and gaseous treatment	Methyl-parathion, Parathion, Diazinon, Cypermethrin.	Pak choi (Chinese cabbage).	1.4 & 2 mg O_3/L concentration; Treatment temperature: 14 & 24 °C; Immersion time of 15 & 30 minutes.	Maximum percentage of reduction with 2 mg O_3/L concentration at 24 °C for 30 minutes treatment: Methyl-parathion – 47.9%, Parathion – 55.3%, Diazinon – 53.4%, Cypermethrin – 61.1%.	(Wu et al. 2007)
	Fenitrothion.	Lettuce, Cherry tomato, Strawberry.	2.5 L/minutes flow rate; Ozone milli bubbling (OMLB): 0.2 mg O_3/L concentration; Ozone micro bubbling (OMCB): 0.5 to 2 mg O_3/L concentration; Immersion time 5 & 10 minutes.	The maximum percentage of reduction with OMCB for 10 minutes: Lettuce – 87%, Cherry tomatoes – 65%, Strawberries – 25%. OMLB does not affect pesticide reduction.	(Ikeura, Kobayashi, and Tamaki 2011)
	Fenitrothion, Benomyl.	Persimmon leaves.	2.5 L/minutes flow rate; Ozone micro bubbling (OMCB): 0.5 to 2 mg O_3/L concentration; treatment time 5 & 10 minutes.	Maximum reduction percentage at 2 mg O_3/L concentration treated for 5 minutes; Fenitrothion – 88%, Benomyl – 62%.	(Ikeura, Hamasaki, and Tamaki 2013)
	Permethrin Chlorofluazuron Chlorothalonil	Chinese white cabbage Green stem PakChoi	500 mg/h flow rate; 15 minutes washing time	Permethrin– 51% Chlorofluazuron – 75% Chlorothalonil – 77%	(Chen, Lin, and Kuo 2013)
	Captan, Boscalid, Pyraclostrobin	Apples	10 ppm concentration, 30 minutes treatment time	Captan – 81–95% , Boscalid – 40–67%, Pyraclostrobin – 20–42%	(Sadło et al. 2017)
	Chlorpyrifos, Cypermethrin	Tomato	0.4 ppm concentration; 30 minutes treatment	Chlorpyrifos – 98%, Cypermethrin – 87%	(Al-Dabbas et al. 2018)
	Difenoconazole, Linuron	Carrot	10 ppm concentration; 2 hours treatment	Difenoconazole – 98% Linuron – 95%	(Souza et al. 2018)
	Azoxystrobin, Chlorothalonil, Difenoconazole	Tomato	3 ppm concentration; 2 L/min flow rate; 30 minutes treatment time	70–90% reduction	(Rodrigues et al. 2019)
Storage in Ozone atmosphere	Azoxystrobin, Bupirimate, Carbendazim, Penconazole, Triadimenol, Trifloxystrobin	Table grapes	0.3 µL/L concentration; 2 °C storage; 36 days storage period	3.6-fold reduction	(Karaca and Karaca 2019)

(continued)

Table 2. Continued.

Method	Pesticide	Sample	Process parameters	Key findings	Reference
Pulsed electric field (PEF)	Methamidophos, Chlorpyrifos.	Apple juice.	Exponentially decaying wave; 1 Hz pulse frequency; 10 µs pulse width; 8–20 kV/cm; 6–26 pulse numbers.	20 kV/cm with 26 pulse numbers tend to give a higher reduction of 76%.	(Chen et al. 2009)
	Diazinon, Dimethoate.	Apple juice.	Exponentially decaying wave; 1 Hz pulse frequency; 10 µs pulse width; 8–20 kV/cm; 60–260 µs.	Maximum reduction at 20 kV/cm with 260 µs; Diazinon – 47.6%, Dimethoate -34.7%.	(Zhang et al. 2012a)
	Pyrimethanil, Vinclozolin, Cyprodinil, Procymidone.	Dry white wine.	Exponentially decaying wave; 0.5 Hz pulse frequency; 10 µs pulse width; 5–20 kV/cm; 0.5–2 ms.	Maximum reduction at 20 kV/cm with 2 ms; Cyprodinil – 49%, Pyrimethanil – 27%, Vinclozolin – 32%, Procymidone – 25%.	(Delsart et al. 2016)
Pulsed electric field (in combination of Ozone & Ultra sonication)	Chlorpyrifos Ethyl, T-Fluvalinate, Cyprodinil, Pyraclostrobin, Malathion	Sour cherries	24.7 kV/cm for 655 µs treatment time with 3 minutes ozone treatment of concentration 20.2 g/m^3 and 35 kHz of ultrasound for 3 min	Chlorpyrifos Ethyl – 91.6%, T-Fluvalinate – 46.76%, Cyprodinil – 88.25%, Pyraclostrobin – 96.7%, Malathion – 82.8%	(Akdemir Evrendilek, Keskin, and Golge 2020)
High-pressure processing	Chlorpyrifos.	Cherry tomato.	25–400 MPa; 30 minutes treatment time; Kerosene as a pressure transmitting medium; 5 & 25 °C operating temperature.	Maximum of 76% reduction at 75 MPa.	(Iizuka, Maeda, and Shimizu 2013)
Ultrasound (in combination with ozone)	Methamidophos, Dichlorvos.	Lettuce.	Ozone flow rate: 25–75 mg/L; bubbling time: 10–60 minutes; U/S frequency 25kHz; U/S power; 1000 W; Bath U/S.	Maximum reduction with 60 minutes treatment time with 75 mg/L; Methamidophos – 80%, Dichlorvos- 67.72%.	(Fan et al. 2015)
Ultrasound (in combination with a low-intensity electrical current)	Captan, Thiamethoxam, Metalaxyl.	Tomato.	Electrical current: 200–1400 mA; Treatment time: 2–10 minutes; Ultrasonic bath of frequency 40 kHz; Ultrasonic probe of frequency 24 kHz.	Maximum percentage @ 1400 mA with 40 kHz U/S bath after 10 minutes treatment; Captan – 94.26%, Metalaxyl – 79.78%, Thiamethoxam – 92.58%.	(Cengiz et al. 2018)
Ultrasonic washing	Difenoconazole, Azoxystrobin, Thiamethoxam, Abamectin B1a And B1b, Tebuconazole	Rape and Grapes	Commercial Ultrasonic dish washer (JBSD3T-Q6)	Maximum of 60% reduction	(Zhou et al. 2019)
	Chlorothalonil, Carbendazim, Pyrazophos	Pak choi (Chinese Cabbage)	Ultrasonic frequency 28 kHz; Ultrasonic power 0.45 W/cm	Chlorothalonil — 74.9%, Carbendazim — 45.7%, Pyrazophos — 24.6%	(Zhu et al. 2019)
Cold Plasma	Paraoxon	Apple	Dielectric Barrier Discharge plasma; 4 kW; Airflow rate 5 L/minutes; Initial pesticide concentration 0.01–100 ppm;	95.9% average percentage of reduction.	(Heo et al. 2014)
	Azoxystrobin, Cyprodinil, Fludioxonil, Pyriproxyfen	Strawberry	80 kV dielectric barrier discharge plasma (DBD) plasma; 5 minutes treatment	azoxystrobin — 69%, cyprodinil — 45%, fludioxonil — 71%, pyriproxyfen — 46%	(Misra et al. 2014)
	Diazinon	Cucumber	Dielectric Barrier Discharge plasma; 0.15–0.75 W; 1–15 minutes treatment; Initial pesticide concentration 25, 50 ppm.	A maximum of 88% reduction at 0.75 W treated for 15 minutes with an initial concentration of 25 ppm.	(Dorraki et al. 2016)

(*continued*)

Table 2. Continued.

Method	Pesticide	Sample	Process parameters	Key findings	Reference
	Boscalid, Imidacloprid	Blueberry	Dielectric Barrier Discharge plasma; 60–80 kV; 0–5 minutes treatment with 24 hour storage in-package; Initial pesticide concentration 25, 50 ppm.	The maximum percentage of reduction at 80 kV for 5 minutes treatment: Boscalid – 75%, Imidacloprid – 80%.	(Sarangapani et al. 2017)
	Chlorpyrifos, Cypermethrin	Mango	Gliding arc discharge; plasma-activated argon vapors; 600 W; Flow rate 2–8 L/minutes; 5–10 minutes treatment time.	Maximum percentage reduction at 5 L/minutes flow rate for 5 minutes treatment: Chlorpyrifos – 74%, Cypermethrin – 62.9%.	(Phan et al. 2018)
	Omethoate, Dichlorvos	Goji berry	Gas surface barrier discharge plasma; 10 kV; 30 minutes treatment time.	Omethoate – 99.55%; Dichlorvos – 96.83%	(Zhou et al. 2018)
	Phoxim	Table grapes	30 minutes PAW preparation time; 10 minutes treatment time; 5 L/min flow rate.	Phoxim – 73.60%	(Zheng et al. 2019)
	Chlorpyrifos	Tomato	Dielectric Barrier Discharge plasma; 5 W plasma power; 6 minutes treatment time.	Chlorpyrifos – 89%	(Ranjitha Gracy, Gupta, and Mahendran 2019b)
	Cypermethrin	Tangerine	Plasma Activated Water; 60 minutes treatment time;Plasma power 125 W; Flow rate of 15 L/min	Cypermethrin – 75%	(Sawangrat et al. 2019)
	Chlorpyrifos	Tomato	Plasma Activated Water; 200 V plasma operating voltage; 10 L/h flow rate; 15 minutes treatment time.	Chlorpyrifos –52%	(Ranjitha Gracy, Gupta, and Mahendran 2019a)

commodity above the critical process parameters. Although these technologies would be favorable as better pretreatments for processes like extraction (Idrovo et al. 2019), drying (Horuz, Jaafar, and Maskan 2017; Wang, Xiao, et al. 2019), and filtration (Chanukya and Rastogi 2016), ensuring a chemical and microbial safety along with the destined action of enhancing mass transfer due to the structural modifications (Paciulli et al. 2019; Terefe, Sikes, and Juliano 2016).

However, the efficiency of the technologies to reduce specific pesticides might vary according to the pesticide structures and concentrations. So, in order to conclude which technology would be giving a promising percentage reduction for a particular pesticide, optimization studies are needed. Also, the preference of the technology would vary according to the process requirements such as the capital and operating cost along with the applicability to the commodity.

Toxicity of metabolites on pesticide degradation by NTP for consumer safety

Though pesticides are potential plant protection agents providing defense to the crops against various predators like insects, fungi, weeds, rodents, and birds, their persistence in the crop poses a threat to the consumer due to its acute or chronic toxic nature. The toxicity of the pesticides is widely mentioned in terms of LD_{50} (Median Lethal dose in mg/kg body weight (bw) of the animal) values, which is the dosage or concentration of the pesticides required to kill 50% of the test population generally rats. Thus, the higher the LD_{50} value, the lesser toxic the pesticide is and vice versa. Table 3 contains the oral LD_{50} values of the studied pesticides tested in male rats proposed by the Food and Agricultural Organization (FAO)/World Health Organization (WHO) specifications for pesticides. Based on the LD_{50} values, the pesticides are widely classified into five categories by WHO such as; class Ia extremely hazardous (LD_{50} value < 5 mg/kg bw), class Ib highly hazardous (LD_{50} value 5–50 mg/kg bw), class II moderately hazardous (LD_{50} value 50–200 mg/kg bw), class III slightly hazardous (LD_{50} value >2000 mg/kg bw), class IV unlikely to cause acute hazard (LD_{50} value >5000 mg/kg bw). Considering the LD_{50} values of the discussed pesticides for reduction by non-thermal technologies, most of the pesticides fall in class II (Metalaxyl, Thiamethoxom, Chlorpyrifos, Dimethoate, Diazinon, Proymidone, chlorpyrifos-thyl, Alsrin, Pirimiphos-methyl,

Table 3. MRLs, reported concentrations in the market samples and reduction percentages of pesticides – a comparative evaluation.

Sl. no	Pesticide name	Non-thermal technique used	Maximum pesticide residue levels (MRL's in ppm)	Maximum pesticide Residue Levels (MRL's in ppm)		Maximum concentration of pesticides in F&V reported (in ppm)	Oral lethal dose in rats (LD_{50}) (mg/kg body weight)
				EFSA	CODEX		
1.	Methamidophos	PEF	30	0.01	0.05	29.47 (Elgueta	30
		O_3	80			et al. 2017)	
2.	Pyraclostrobin	PEF	42	0.05	0.01	1.25	>5000
		PEF + O_3+U/S	97				
3.	Metalaxyl	Gamma	80	0.01	0.05	1.76	375*
4.	Thiamethoxam	Gamma	93	0.01	0.01	0.71	1563
5.	Chlorpyrifos	PEF	76	0.01	0.01	9.83 (Mebdoua et al. 2017)	229
		O_3	98				
		Gamma	91				
		HPP	76				
		GAP	74				
		PAW	52				
		DBD	89				
6.	Dimethoate	PEF	48	0.02	0.05	7.88 (Fosu et al. 2017)	310
7.	Diazinon	PEF	35	0.01	0.01	0.12 (Khan et al. 2019)	325
		Gamma	90				
		GAP	88				
8.	Pyrimethanil	PEF	27	0.01	0.05	0.1 (Lozowicka, Abzeitova, and Sagitov 2015)	4149
9.	Vinclozolin	PEF	32	0.3	NR	0.5 (Park	>15000
10.	Procymidone	PEF	25	0.01	0.5	4.7 et al. 2015)	1450
11.	Azoxystrobin	O_3	90	0.01	0.01	7.0	>5000
		U/S	72				
12.	Cyprodinil	PEF	49	0.02	0.05	5.82 (Elgueta	>2000
		PEF + O_3+U/S	88			et al. 2017)	
13.	Boscalid	O_3	67	0.01	0.6	8.73	>5000*
14.	Chlorpyrifos-ethyl	PEF + O_3+U/S	92	0.05	0.01	4.6 (Illyassou et al. 2018)	229
15.	τ-Fluvalinate	PEF + O_3+U/S	47	0.01	NR	>0.01 (Santarelli et al. 2018)	>2000*
16.	Malathion	PEF + O_3+U/S	83	0.02	0.01	4.0 (Li et al. 2018)	6156
		Gamma	35				
17.	Carbendazim	O_3	38	0.1	0.02	3.4	>10000*
		U/S	25				
18.	Aldrin	Gamma	30	0.01	0.05	0.042 (Liu et al. 2016)	64
19.	Endrin	Gamma	4	NR	0.05	0.37 (Oluwaseyi et al. 2019)	40
20.	Heptachlor epoxide	Gamma	43	0.01	0.01	0.13 (Ahmed et al. 2016)	40–260
21.	Pirimiphos-methyl	Gamma	100	0.01	0.5	0.43 (Ibrahim et al. 2018)	1260
22.	Cypermethrin	O_3	87	0.05	0.01	13.92 (Chen et al. 2011)	360
		Gamma	28				
		GAP	63				
23.	Fenitrothion	O_3	75	0.01	0.5	0.02 (Sapbamrer and Hongsibsong 2014)	1700
24.	Benomyl	O_3	75	0.1	2.0	0.99 (Abdi and Sobhan Ardakani 2019)	>5000
25.	Captan	O_3	95	0.03	0.05	0.36 (Larsson et al. 2018)	>5000
		U/S	94				
26.	Difenoconazole	O_3	98	0.05	0.02	81.5 (Akhtar, Yaqub, and Hamid 2018)	1453
		U/S	82				
27.	Chlorothalonil	O_3	90	0.01	0.01	14.33 (Al-Nasir et al. 2020)	> 5000
		U/S	75				

28.	Trifloxystrobin	O_3	52	0.01	0.02	0.16 (Lozowicka et al. 2016)	>5000
29.	Triadimenol	O_3	61	0.01	0.05	5.1 (Lima et al. 2017)	700–1500
30.	Dichlorvos	Gamma	80	0.01	NR	1.58 (Yu et al. 2016)	57–108
31.	Phorate	Gamma	78	0.01	0.1	0.12	3.7
32.	Tebuconazole	Gamma	88	0.02	0.02	7.8 (Loughlin et al. 2018)	4000
33.	Paraoxon	DBD	96	0.01	0.2	0.49 (Li et al. 2011)	2
34.	Imidacloprid	DBD	80	0.05	0.05	1.65 (Akhtar, Yaqub, and Hamid 2018)	424

*Source of the LD_{50} values are from Europian Union Pesticide database while others are from FAO/WHO specifications.

Cypermethrin, Fenitrothion, Difenoconazole, Triadimenol, Dichlorvos, Imidacloprid) followed by class IV pesticides (Pyraclostrobin, Vinclozolin, Azoxystrobin, Boscalid, Malathion, Carbendazim, Benomyl, Captan, Chlorothalonil, Trifloxystrobin). Though the studied class II and IV pesticides are moderately and slightly hazardous, a higher concentration may lead to chronic toxicity. Considering the toxicity level, these pesticides were considered for reduction using non-thermal technologies. When the pesticide concentration is reduced from the food commodity, the risk of consumer exposure to toxic compounds ingestion considerably reduces. Nevertheless, it is also important to assess the by-products or metabolites or intermediates of the pesticides when subject to degradation as the toxicity of most of the parent pesticide compounds differs from that of by-product metabolites. But, many challenges evolved in analyzing or detecting the degraded pesticide products. Some of the challenges include inadequate commercial standards of the degraded products, intricacy in the compounds due to the presence of food matrix, the possibility of a number of products via varying pathways that are difficult to be predicted (Misra et al. 2014). Because of these challenges, most studies on non-thermal technologies for pesticide reduction have not performed the screening and detection of the degraded pesticide metabolites in the product after the treatment.

Few studies (except on ultrasonication and ɤ-irradiation) attempted to detect the metabolites through complete ion spectrum screening and discussed their toxicity after degradation. Zhang et al. (2012a) detected water-soluble inorganic ions SO_4^{2-}, CO_4^{2-}, PO_4^{3-}, NO_3^- after degradation of diazinon and dimethoate by the pulsed electric field (PEF) and explained the effectiveness and desirability of the treatment for ensuring consumer safety. Chen, Lin, and Kuo (2013) analyzed the toxicity of the pesticide permethrin, chlorfluazuron, and chlorothalonil after the ozone washing treatment using the response of fluorescence bacteria and found that the toxicity was significantly reduced after the treatment. Similarly, Zhou et al. (2018) also studied the toxicity of omethoate and dichlorvos after gas barrier discharge plasma treatment. However, the author found that the toxicity increased for the initial plasma treatment time of 0–6 min, after which it was depleted. The reason behind this is the identified metabolite/intermediates produced, i.e., O, O dimethyl phosphoric esters (P_1); O, O, O trimethyl phosphorothioate (P_2); O, O, S trimethyl phosphothioate (P_3); N-methyl-2-sulfanyl acetamide (P_4) and 2, 2, dichlorovinyl O-methyl phosphate (P_5). Except for P_3, other intermediates were less toxic than the parent compound (Hollingshaus et al. 1981). As the reaction proceeds, P_3 degraded further to the other innocuous metabolites; thereby, the toxicity initially arose and then reduced. The other studies on cold plasma degradation of pesticides have also revealed the efficiency of the process in assuring toxicity reduction. Ranjitha Gracy, Gupta, and Mahendran (2019b) identified the presence of a secondary metabolite 3, 5, 6 Trichloro pyridinol (TCP) of chlorpyrifos after 6 min of 5 W dielectric barrier discharge plasma treatment. The LD_{50}

value of TCP was 800 mg/kg body weight, which is lesser than that of the parent pesticide, i.e., the chlorpyrifos and the primary metabolite, chlorpyrifos oxon. The process was found to be capable of degrading the parent and primary metabolite to give a lesser toxic secondary metabolite, which exhibits its ability to degrade the secondary metabolite further by intensifying the process parameters leading to complete mineralization. Likewise, Dorraki et al. (2016), Sarangapani et al. (2017), and Zheng et al. (2019) identified benign products after plasma degradation of diazinon, boscalid, imidacloprid, and phoxim, respectively. Degradation of boscalid gives mono and dihydroxylated products along with carboxylic acids, whereas imidacloprid degrades to 6-chlonicotinic acid and 6-chloronicotinic aldehydes. Phoxim metabolizes to 2-hydroxyimino-2-phenylacetonitrile along with O-diethyl-O-α- cyano benzylidene amide on reaction with the hydroxyl radicals and other reactive oxygen species of plasma applied. Though these degraded by-products were harmless, some metabolites like diazoxon, paraoxon, methyl paraoxon from diazinon, parathion, and methyl parathion degradation respectively using ozonized water have lower LD_{50} values than its parent compounds, thereby with increased toxicity. However, as they are also mostly polar and highly unstable, their removal on simple water washing is decisive. Misra et al. (2014) also proposed a mechanism for degradation of fludioxonil on plasma treatment based on the detection of a metabolite 2, 2, difluorobenzo [1, 3], dioxole 4-carboxylic acid, which was again a class IV compound with LD_{50} of $>$ 5000 mg/kg body weight (FAO/WHO).

Unlike the above studies, Souza et al. (2018) and Iizuka, Maeda, and Shimizu (2013) did not find any intermediate degraded difenoconazole products, linuron, and chlorpyrifos while treating with ozonized water and high-pressure processing, respectively. This further justifies the supremacy of the non-thermal technologies for pesticide reduction. In some studies, the degradation reactions proposed by the reactions with simple aqueous pesticide solutions were used to predict the by-products and metabolites. However, it is necessary to identify the metabolites in pesticide degradation studies in fruits and vegetables in concern with all non-thermal technologies' safety aspects.

Supremacy of non-thermal technology over thermal technology

Thermal processing refers to the application of heat on fruits and vegetables, commonly done through pressure cooking, ordinary cooking, sterilization, pasteurization, frying, ohmic heating, radio frequency heating, canning, and microwave cooking (Ma et al. 2011). Pesticide residue such as tetrachlorvinphos (Fahey, Nelson, and Ballee 1970), azinphos-methyl (Ong et al. 1996), organophosphorus and organochlorines (Kaushik, Satya, and Naik 2009), esfenvalerate (Zabik et al. 2000), dimethoate, malathion (Abou-Arab 1999), carbophenothin, parathion, cypermethrin, and azoxystrobin (Lentza-Rizos, Avramides, and Kokkinaki 2006) in fruits and vegetables are reduced by thermal treatment. But, organoleptic changes, alternation in nutritional properties such as protein denaturation, loss of heat liable mineral, and vitamin, volatile flavors were observed (Abou-Arab 1999; Ramirez et al. 2009).

The cooking of contaminated tomatoes with organophosphorus and organochlorines pesticide residues at 1 ppm at 100 °C for 30 min reduced the level of contamination up to 81.6% and 30.7%, respectively (Kaushik, Satya, and Naik 2009). Whereas, 95% of organophosphorus and organochlorine pesticide residue dissipation was attained by 1 kGy gamma irradiation in cut vegetables like capsicum, tomato, and cucumber (Chowdhury et al. 2014). This outcome is due to the higher stability of organochlorine pesticides to thermal treatment (Abou-Arab 1999). Gas-phase surface discharge plasma treatment reduced organophosphorus pesticide to 96.83–99.55% in *Lycium barbarum*, and GPSD plasma did not induce any changes in the fruit quality (Zhou et al. 2018). Other than gamma irradiation and cold plasma, no other non-thermal technologies studied for same pesticide residue and similar fruits and vegetables for comparison. Hence, comparison was restricted only to gamma irradiation and cold plasma on organophosphorus and organochlorine pesticide residue dissipation. However, non-thermal technologies are comparatively providing, better pesticide residue reduction in fruits and vegetables by retaining organoleptic and nutritional properties.

Conclusion

Growing global demand for pesticide-free foods necessitates dissipation technologies, which will degrade the pesticides into its innocuous metabolites without causing significant changes in the physicochemical and organoleptic properties of the treated commodities, mainly the fruits and vegetables, as they are rich in sensitive nutritional profile. The pesticide reduction using non-thermal technologies like pulsed electric field (PEF), gamma irradiation, ozone, ultrasonication, high-pressure processing, and cold plasma showed the potential and the scope of these technologies for incurring lesser residual pesticides presence under the maximum permissible residual limit (MRLs). Each technology surpasses the limitations of others due to their varying mechanisms of action over the pesticides. However, the appropriateness of the technology for maximum pesticide reduction depends on the product and the pesticide characteristics. Thus, extensive research on these technologies for a wide range of pesticides in the agricultural commodities is mandated to understand their applicability in a large-scale operation.

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