Articles

2015

The Contribution of Non-Thermal and Advanced Oxidation Technologies Towards Dissipation of Pesticide Residues

N. Misra
Technological University Dublin, misra.nrusimhanath@tudublin.ie

Recommended Citation

The contribution of non-thermal and advanced oxidation technologies towards dissipation of pesticide residues

N.N. Misra [1],*

[1] *School of Food Science and Environmental Health, Dublin Institute of Technology, Dublin 1, Ireland*

* Corresponding author; Present address: GTECH (R&D), General Mills India, Hyde Park, Mumbai-76, India. E-mail: misra.cftri@gmail.com; Tel (☎): +91 22 4203 1566

Abstract

Background

The use of pesticides has stabilised the food production to a great extent and their usage cannot be avoided anymore. Nevertheless, common food processing operations always allowed dissipating pesticide residues in foods to some extent. Within the food science community and the food processing sector, non-thermal food technologies are being researched and commercialised at a great pace over the past three decades.

Scope and Approach

In this review we provide a critical analysis of the literature pertinent to the fate of pesticide residues during non-thermal processing of solid and liquid foods. We also identify the opportunities for further development and provide guidelines for future research. The non-thermal technologies considered include high pressure processing, pulsed electric fields and advanced oxidation processes (AOPs) such as ozone, ultrasound, ultraviolet light, ionising radiation, non-thermal plasma, and their synergy.

Key Findings and Conclusions

In general, information about the fate of pesticides during non-thermal processing of foods is still very scarce. A considerable number of studies have reported the efficacy of AOPs for breakdown of pesticides in food and water; however, information regarding the mechanism of action and toxicity is limited. For industrial adoption and commercial success, researchers are advised to focus their studies through an economic lens.

Keywords: advanced oxidation process; cold plasma; ultrasound; ozone; irradiation; HPP

Preprint submitted to Trends in Food Science & Technology

1. Introduction

The use of pesticides in agriculture has undoubtedly stabilised the crop production patterns within past century. Despite the benefits in agricultural production, their adverse effects on environment and living organisms remain a major concern. These problems will significantly magnify in next few decades with the increasing demand for food by the growing population and the necessity to maintain sustainability in agricultural production and food processing sectors. Pesticide poisoning, globally, and especially in developing countries has remained a concern since decades. The genotoxic effects of pesticides and their carcinogenicity is well-established. The chronic diseases in humans associated with pesticide residues in food and water was recently reviewed in detail by Mostafalou and Abdollahi (2013). On one hand, consumers are inclining more towards consumption of fresh fruits and vegetables with increasing awareness regarding their health benefits. On the other hand, they are becoming increasingly concerned about the risk of microbial contamination and pesticides. Until a decade ago, the extensive use of hazardous pesticides was reported in Central America (Wesseling, Corriols, & Bravo, 2005). The EU commission is also constantly taking resolutions to achieve crop production patterns with low pesticide input. This reflects in the EC thematic strategy on the sustainable use of pesticides (EC, 2010). Several measures, including legislation, agricultural standardisation and farmer education, have been implemented by governmental bodies of many countries to solve the issue of pesticide residues. Current research in nanotechnology has helped development of nano-particle pesticide applications to impart dose controllability and stability, thereby setting new standards in precision agriculture. While such novel class of nano-pesticides do not wash off readily and therefore are effective, they do pose a new order of risks to consumers of treated plants as the pesticides would consequently be more persistent on the plant (Coles & Frewer, 2013). In-depth information regarding the characterisation of pesticides, their regulatory aspects, and a comprehensive list of references and electronic links for details on agrochemicals in food systems can be found in Greene and Pohanish (2005).

Guidelines for pesticide applications to standing crops and appropriate harvest times do exist. At the same time, the use of pesticides is poorly regulated and often dangerous; their easy availability also makes them a popular method of self-harm, especially in developing countries. Additionally, harvests are often rushed to the market, leaving large amounts of pesticide residues on vegetables and fruits (Chen, Lin, & Kuo, 2013). Moreover, for controlling pests in short periods, farmers generally apply higher doses than those recommended. Thus, there are high chances that the agricultural produce falls into the hands of end consumers with pesticide levels in excess of safe limits. The problem is especially of importance to fresh fruits and vegetables which are often consumed without washing or with minimal processing. However, pesticide residues on other food classes such as cereal and pulse grains cannot be ignored. Likewise, the European Water Framework Directive 2000/60/EC identifies

Preprint submitted to Trends in Food Science & Technology

33 priority substances that present high toxicity and bioaccumulation, including pesticides such as atrazine, diuron, isoproturon, alachlor, pentachlorophenol, and chlorfenvinphos.

Pesticide-free, organic fruits and vegetables have set a new trend in both developed and developing countries. However, only a minor population is willing to pay for such produce. Household food processing operations such as washing and peeling in general, are effective at eliminating pesticide residues to a great deal (Bonnechere, Hanot, Bragard, Bedoret, & van Loco, 2012). Such is also the case with conventional industrial scale food processing. Several authors, including Kaushik, Satya, and Naik (2009), Keikotlhaile, Spanoghe, and Steurbaut (2010) and Bajwa and Sandhu (2014) have extensively reviewed the fate of pesticides during handling and following common food processing operations at household as well as industrial scale. These authors have reviewed the effects of many common unit operations such as baking, fermentation, malting, milling, drying and thermal processing.

Within the past two decades, research in food science has largely focused on development of non-conventional thermal and non-thermal technologies, in light of the undesirable effects associated with the application of heat treatments to food matrices (Misra, Kadam, & Pankaj, 2011). Products processed by high-pressure processing (HPP) technology and pulsed electric field (PEF) processing are already available in the market. Other technologies such as ultrasonication, ozonation and cold plasma are being researched at great pace; perhaps, these could be envisaged at the verge to commercialisation. These approaches are integrated within the framework of advanced oxidation processes (AOPs). AOPs can be broadly defined as near-ambient temperature treatment processes based on highly reactive radicals, especially the hydroxyl radical, as the primary oxidant. For the fundamentals and underlying principles of the non-thermal technologies, the readers are redirected to the recent book by Zhang, Barbosa-Cánovas, et al. (2010). Irrespective of the approach employed, the main aim of developing new technologies is to provide safe and appealing foods to the consumers within a sustainable framework. Having said this, it obviously becomes important to evaluate the efficacy of these (future) technologies in ensuring food safety, not only from a microbiological standpoint, but also chemical.

In this review, our goal is to discuss and critically analyse the chemical safety assessed on the basis of pesticide dissipation potential of the non-thermal technologies. This review does not address the subject of microbial toxins, allergens, packaging additive migrants or processing contaminants. We hope that this review will convince food scientists, environmentalists as well as policy makers, that non-thermal and AOPs have ample potential to contribute towards pesticide dissipation in foods and sustainability within the modern agricultural production and food processing framework.

The structure of the present paper is the following. In the next section we review the effects of high-pressure and pulsed electric field processes on pesticide residues, followed by other AOPs (advanced

3

oxidation processes), commencing from the extensively researched ozone processing. This is succeeded by a critical discussion of cold plasma, ionising radiation, ultrasonication and combined or miscellaneous approaches. Besides discussing the effects of the processes and underlying reaction mechanism, where available, we also discuss the effects of process parameters and underlying challenges. Finally, we lay directions for future research and end with conclusions.

2. High Pressure Processing (HPP)

In HPP the food product inside a hermetically sealed flexible pouch is introduced into a pressure vessel and exposed to high pressures (~300-800 MPa for 3-5 minutes) using a pressure transmitting fluid (typically water). HPP is a purely physical technique governed by the isostatic principle of pressure transmission, which states that pressure is instantaneously and uniformly transmitted throughout a sample irrespective of its presence inside a sealed package or direct contact with the pressure transmitting medium. HPP has been extensively researched within past twenty years considering its ability to inactivate pathogens at room temperature and retain the organoleptic characteristic and nutritional quality of foods (Huang, Hsu, Yang, & Wang, 2014). Advances in HPP technology have been comprehensively reviewed (Norton & Sun, 2008; Rastogi, Raghavarao, Balasubramaniam, Niranjan, & Knorr, 2007). HPP has already become a commercially implemented technology, spreading from its origins in Japan, and slowly introduced into other countries such as USA and Europe (Evert-Arriagada, Hernández-Herrero, Guamis, & Trujillo, 2014). Interestingly, however, the fate of pesticide residues during HPP remained untouched until recently, when it was shown that high hydrostatic pressure (HHP) processing can successfully reduce hydrophobic pesticide residues.

Iizuka, Maeda, and Shimizu (2013) reported the removal of the hydrophobic pesticide, chlorpyrifos [O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothionate] from cherry tomatoes following HPP. The group concluded that the optimum processing conditions for reducing chloropyrifos residues on cherry tomatoes was around 75 MPa for 30 minute at 5 °C, with a removal rate of about 75% (from 7.6 to 2.0 mg/kg). Further, HPP was reported to be more efficient than rinsing with water or ultrasonication. HPP being a physical technique is very unlikely to cause breakdown of pesticides. Thus, the absence of toxic intermediates such as chloropyrifos oxon (which has higher toxicity) is also confirmed (Iizuka & Shimizu, 2013). Furthermore, the pesticide residue was shown to migrate into the surrounding fluid (water). From a mechanistic point of view, the weakening of hydrophobic interactions at high pressures explains the migration of hydrophobic pesticides from produce surface (Iizuka, Yahata, & Shimizu, 2013). A higher removal has been achieved (starting from 0.50±0.08 mg/kg) with ethanol as the filling media during high pressure treatments compared to water under identical process conditions. This is justifiable as the hydrophobicity of ethanol is relatively higher

than water. Despite the above studies, there exists only little information about the fate of pesticides during HPP. Extensive work is yet to be carried out to understand the fate and dissipation mechanism of pesticides during HPP, including comparison between hydrophobic and hydrophilic pesticides. Considering that HPP is a commercial technology, at least toxicity studies of the treated samples is likely to give clear indication regarding the overall safety of intermediates formed, if any.

3. Pulsed Electric Field Processing (PEF)

PEF processing involves the application of very short electric pulses, typically of 1-100 μs duration at electric field intensities in the range of 0.1 kV cm^{-1} up to 40 kV cm^{-1} to induce reversible/irreversible permeabilization in plant, animal and microbial cells. The high intensity electric pulses for PEF processing are generated by the switched discharge of a capacitor bank via a discharge circuit, whose configuration governs the shape of the time-varying electric pulse. PEF processing has been successfully employed for inactivation of vegetative micro-organisms and enzymes in fruit juices and milk. It has also found applications in large-scale disintegration of plant raw materials for improvement of extraction efficiency and mass-transfer rates.

We identified only two studies reporting the degradation of pesticides during PEF processing. The first report was by Chen, et al. (2009), where the successful degradation of methamidophos (O,S-di-methyl phosphoramidothioate) and chlorpyrifos spiked into apple juice with the latter being more labile to the process was reported. The electric field strength and pulse number were both found to be important factors governing the pesticide degradation. In another independent study, Zhang, Hou, et al. (2012) reported the successful degradation of diazinon [*O,O*-Diethyl *O*-(4-methyl-6-(propan-2-yl)pyrimidin-2-yl) phosphorothioate] and dimethoate [O,O-dimethyl S-(2-(methylamino)-2-oxoethyl) dithiophosphate] added to apple juice. The authors indicated that the electric field strength and treatment time were important parameters governing the degradation efficacy. On the positive side the authors did not observe any harmful intermediates through mass-spectrometry studies and hypothesised the complete degradation into soluble products. Toxicity studies based on photobacterium bioassay also confirmed the mitigation of sample toxicity.

Zhang, Hou, et al. (2012) associated the pesticide degradation to the reaction with hydrogen peroxide and hydroxyl radicals formed during the PEF treatments. It is worth mentioning that the formation of these radicals is promoted by the electrochemical reactions resulting from the release of Fe^{2+}/Fe^{3+} due to corrosion of the electrodes. On the other hand, Chen, et al. (2009) mentioned that PEF could increase the vibration and rotation of molecules, thereby facilitating the degradation; however, they did not study the degradation pathway. Kinetic modelling in the above studies revealed that the degradation pathways in PEF vary depending on the chemical nature of pesticides. However, no firm

Preprint submitted to Trends in Food Science & Technology

conclusions can be made unless the research community is willing to undertake studies to unravel the chemical pathways of degradation.

4. Ozone Processing

Ozone is a well-known gaseous chemical agent capable of oxidising a variety of organic and inorganic compounds in gaseous phase, on solid substrate and aqueous solutions, either by direct attack, or through a radical mediated mechanism involving the hydroxyl radical. It also enjoys the GRAS status and is approved by the FDA as a food additive (Segat, et al., 2014). Industrial scale production of ozone involves electrical discharges in oxygen or air from a corona source or as dielctric barrier discharge (DBD). The discharge generates energetic electrons, which dissociate oxygen molecules by direct impact. The resulting singlet oxygen ($O^{\bullet}$) combines with oxygen molecule (O_2) via a three body interaction to form ozone (O_3). It should be noted that while this simple scheme explains ozone production in pure oxygen, the reactions leading to production of ozone in air could be quite complex with the involvement of over 50 reactions. Ozone has been recommended in the horticulture industry for both ethylene removal and antimicrobial purposes and these aspects have been reviewed by several researchers (Karaca & Velioglu, 2007; Khadre, Yousef, & Kim, 2001). The fundamentals and applications of ozone based technologies in food processing are extensively reviewed in a recent book (O'Donnell, Tiwari, Cullen, & Rice, 2012). About two decades ago, the degradation of pesticides during aqueous ozonation was reviewed by Reynolds, Graham, Perry, and Rice (1989). For brevity, we provide a discussion of the contemporary studies, which investigate effectiveness of ozone towards pesticide degradation in fruits and vegetables. We also comment upon the role of important process and product parameters on the efficacy of treatment.

Within recent years, several studies have reported effective degradation of pesticide residues in fruits and vegetables by ozone, both in gas phase and as dissolved ozone. In an early study, Ong, Cash, Zabik, Siddiq, and Jones (1996) reported the breakdown of methyl-azinophos, captan and formetanate hydrochloric acid on the surface of apple using ozonated water. Hwang, Cash, and Zabik (2001) also recorded 56-97% reduction of mancozeb residues on apple following ozone treatments. Efficient reduction of methyl-parathion, parathion, diazinon and cypermethrin in leafy vegetable using ozonated water washing is also confirmed, and the effectiveness is reported to be mainly influenced by the dissolved ozone levels and temperature (Wu, Luan, Lan, Hung Lo, & Chan, 2007; Wu, Luan, Lan, Lo, & Chan, 2007). Ikeura, Kobayashi, and Tamaki (2011a) studied the removal of fenitrothion from lettuce, tomatoes and strawberries using continuous ozone micro-bubbled solution and reported that the residual fenitrothion was efficiently removed from the vegetables. A summary of the recent studies investigating the use of gas phase and dissolved ozone for dissipation of pesticide residues on fresh produce are summarised in Error! Reference source not found..

Table 1 Summary of recent studies on degradation of pesticide residues in foods by ozone.

Pesticide	Matrix	Process	Analytical Method	Salient Results	Reference
Fenitrothion	Lettuce	O_3 millibubble and microbubble treatment using dechlorinated water @ 0.2 and 2.0 ppm for 0, 5, 10, 15 and 20 min; Water temperatures- 15, 20, 25, and 30 °C	Acetone-Hexane extraction on diatomaceous column, followed by GC-MS estimation.	Bubbling O_3 microbubbles at 30 °C was most effective with only 32% residual FT, followed by washing with O_3 microbubbles (54%) and millibubbles (69% residue). No adverse effects on colour and texture.	Ikeura, Kobayashi, and Tamaki (2013)
fenitrothion	Cherry Tomato	O_3 millibubble and microbubble treatment using dechlorinated water @ 0.2 and 2.0 ppm for 0, 5, 10, 15 and 20 min; Water temperatures- 15, 20, 25, and 30 °C	Acetone-Hexane extraction on diatomaceous column, followed by GC-MS estimation.	Bubbling O_3 microbubbles at 30 °C was most effective with only 52% residual FT, followed by washing with O_3 microbubbles (59%) and millibubbles (69% residue). No adverse effects on colour and texture.	Ikeura, Kobayashi, et al. (2013)
permethrin, chlorfluazuron and chlorothalonil	Chinese white cabbage; green-stem bok choy (*Brassica rapa*)	Domestic-scale O_3 vegetable cleaner developed in-house. O_3 production rates: 250 and 500 mg/h; Treatment times: 15, 30 and 45 minute	Acetone-petroleum ether-dicholoromethane extraction and GC-ECD quantification.	>80% removal of pesticides at 500 mg/h ozonation for 30 min. Following washing, all pesticide residuals met the standards for pesticide residue limits in foods.	Chen, et al. (2013)
fenitrothion and benomyl	Persimmon leaves (red and green)	0.2, 0.5, 1.0 and 2.0 ppm ozone microbubbles; Treatment time: 0, 5, 10 and 15 min; Water temperature- 20 °C	Ethyl Acetate-Hexane-Dichloromethane extraction and HPLC-UV quantification.	Continuous O_3 microbubbling at 2.0 ppm dissolved O_3 was most effective. No adverse effects on colour and texture.	Ikeura, Hamasaki, and Tamaki (2013)
fenitrothion	Lettuce, Cherry Tomato and Strawberry	Dipping produce in 500 ppm solution for 1 min; 2.0 ppm O_3 concentration from a decompression type and gas-circulation type generator; Treatment Times: 0, 5 and 10 min; Water temperature- 20 °C	Acetone-Hexane extraction on diatomaceous column, followed by GC-MS estimation.	Using decompression type [DT] and gas-water circulation type [GWCT] generators, after 10 min, residual reached 33 and 45% in Lettuce, 84 and 95% in Cherry Tomato, 62 and 87% in strawberries respectively. The DT was more effective than the GWCT O_3 generator.	Ikeura, et al. (2011a)
fenitrothion	Lettuce, Cherry Tomato and Strawberry	O_3 millibubble and microbubble treatment using dechlorinated water @ 0.2 ppm and 0.5, 1.0, or 2.0 ppm respectively for 0, 5 and 10 min. Water temperature- 20 °C	Acetone-Hexane extraction on diatomaceous column, followed by GC-MS estimation.	Up to 52% reduction of FT in Lettuce, 35% in Cherry Tomatoes, and 25% in Strawberries with 2.0 ppm bubbling O_3 microbubbles. O_3 microbubbles are more effective than millibubbles.	Ikeura, Kobayashi, and Tamaki (2011b)

Preprint submitted to Trends in Food Science & Technology

Mixture of boscalid, iprodione, fenhexamid, cyprodinil, and pyrimethanil solutions	'Thompson Seedless' table grape	Treatment in a cold storage for up to 36 days with 0.300 μL/L gaseous ozone obtained from a corona discharge	Extraction in methyl-*tert*-butyl ester (MTBE), followed by GC-MS analysis in scan mode operation.	Up to 46.2%, 23.9%, 64.5%, 34.7%, and 51.6% reduction in concentration of Boscalid, Iprodione, Fenhexamid, Cyprodinil, and Pyrimethanil respectively was recorded. Reductions of Boscalid and Iprodione in ozone were not significantly different from air storage.	Karaca, Walse, and Smilanick (2012)
chloropyrifos ethyl, tetradifon and chlorothalonil	Lemon, Orange and Grapefruit	Ozonation @ 4, 6 and 10 ppm in tap water for 5 min; Water temperatures- 10, 20, and 40 °C	QuEChERS method (Acetonitrile separation and cleaning), followed by GC-MS estimation	Complete removal of chlorothalonil and chloropyrifos ethyl from orange and grapefruit in 5 min. Increasing temperature had a negative effect on pesticide removal.	Kusvuran, Yildirim, Mavruk, and Ceyhan (2012)
azinphos-methyl, captan, formetanate hydrochloride	Golden Delicious Apple and Apple sauce	Ozone wash @ 0.25 mg/L for 15 min	Azinphos-methyl and Captan extraction in hexane and GC-NPD and GC-ECD detectors. Formetanate-HCl extraction in acetonitrile and HPLC-UV detection	Up to 75%, 72% and 46% reduction in azinophos-methyl, captan and formetanate-HCl residues respectively, with ozone wash. A significant reduction in processed apples was also noticed.	Ong, et al. (1996)
boscalid, iprodione, fenhexamid, cyprodinil, and pyrimethanil	Thompson seedless grape	Ozonation for 2 h at a constant [O_3] of 900±12 ppmv obtained from a ultraviolet ozone generator	Extraction in methyl-*tert*-butyl ester (MTBE), GC-MS of the non-polar phase; LC-MS of the polar phase.	Decrease in residue concentration was observed for only fenhexamid, cyprodinil and pyrimethanil.	Walse and Karaca (2011)
chlorpyrifos	Lychee (*Litchi chinensis*)	Dipping in ozonated water at concentrations of 2.2, 2.4, 3.4 and 3.2 mg/L from a corona discharge for 10, 20, 30 and 60 min	GT-pesticide test kit (Enzyme inhibition method)	A 10% removal of chlorpyrifos was achieved. The eating quality of lychee was not acceptable.	Whangchai, Uthaibutra, Phiyanalinmat, Pengphol, and Nomura (2011)
chlorpyrifos	Lychee (*Litchi chinensis*)	Gaseous ozone (O_3) treatment at [O_3] of 80, 160, 200, 240 mg/L from a corona discharge for 10, 20, 30 and 60 min	GT-pesticide test kit (Enzyme inhibition method)	Up to 45% removal of chloropyrifos in 60 min of treatment. Fumigation was more effective than ozone water wash in removing pesticide residue.	Whangchai, et al. (2011)
methyl-parathion,	Pak Choi (*Brassica*	Continuous ozonation at 1.4 and 2.0 mg/l	Acetone extraction,	Rinsing at 2.0 mg/l initial dissolved ozone	Wu, Luan, Lan, Hung

Preprint submitted to Trends in Food Science & Technology

parathion, diazinon, and cypermethrin	*rapa*)	dissolved ozone concentrations, at temperatures of 14 and 24 °C for 15 and 30 min	dichloromethane or petroleum ether (for cypermethrin) for clean-up; GC-MS analysis	for 30 min increased the pesticide removal efficiency to 45-61%. Reduction efficiency increase with increase in temperature.	Lo, et al. (2007), Wu, Luan, Lan, Lo, et al. (2007)
fenhexamid, cyprodinil, pyrimethanil, pyraclostrobin, iprodione and boscalid	Thompson seedless grape	Fumigation of berries with 10000 µL/L ozone for 1 h, obtained from a corona discharge	Acetonitrile and solid-phase extraction followed by GC-ECD analysis.	Residues of fenhexamid, cyprodinil, pyrimethanil, and pyraclostrobin were reduced by 68.5, 75.4, 83.7, and 100.0%, respectively @ 10,000 µL/L O_3 for 1 h; Reduction of iprodione and boscalid was not significant.	Gabler, Smilanick, Mansour, and Karaca (2010)
Diphenylamine, carbendazim, and chlorothalonil	Apple peel	Treatment Times: 0, 5, 10, 15 and 25 minute; O3 concentrations: 0, 4, 8, 12, 16, 18 mg/L; Temperature: 35 °C, pH 6.35	Acetonitrile-Acetone extraction, followed by GC-FPD detection	The degradation rate increased with increase in pesticide concentration.	Jijun, Zhonghai, Haiyan, Jing, and Yinghong (2011)

In majority of the studies, the kinetics of pesticide degradation has been approximated to follow a direct attack and therefore first-order kinetics with respect to the pesticide concentration has been reported. The action of ozone has been suggested to follow Criegee reaction mechanism for many pesticides (Criegee, 1975). The addition of ozone to carbon-carbon double bonds of pesticide molecules to form ozonide is a classic example of the 1,3 dipolar addition class of organic reactions. This reaction is initiated from the electrophilic end of the ozone molecule. The ozonide is subsequently reduced when it comes in contact with water to form hydrogen peroxide. In some cases (usually for liquid and condensed phase reactions) the carbonyl compound and the Criegee intermediate produced upon ozonolysis of an alkene may also recombine to form a secondary ozonide (Al Rashidi, Chakir, & Roth, 2013).

Al Rashidi, et al. (2013) identified the compound 4-chlorophenyl 3,4-dimethoxyphenyl methanone (CPMPM) following ozonation of dimethomorph. The authors proposed the reaction scheme provided in **Figure 1** to elucidate the ozonolysis. Here, it may be noted that the double bond is most susceptible to ozone attack, leading to the formation of a primary ozonide which being unstable dissociates into a stable compound and the corresponding Criegee intermediate. The Criegee intermediate can undergo further decomposition via. O-atom elimination, ester channel, hydrogen peroxide channel, or it might stabilise following collision with another body.

Ozonation for pesticide dissipation is a typical example of gas absorption with a chemical reaction, which may be affected by the reaction kinetics or by mass transfer, or both. Therefore, all the process variables which affect these two processes will govern the efficacy of the ozone treatment. We will

Preprint submitted to Trends in Food Science & Technology

now provide an account of some important variables governing the efficacy of gas phase as well as liquid phase ozone treatments.
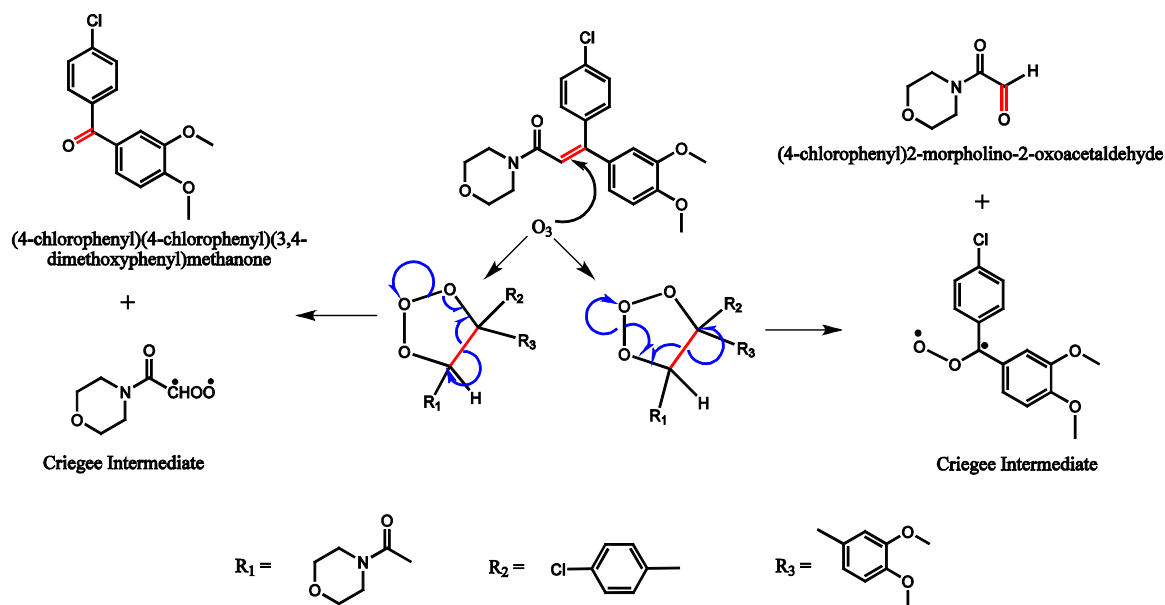

Figure 1 Mechanism of ozonolysis of dimethomorph and the corresponding Criegee intermediates. Adapted from Al Rashidi, et al. (2013) by courtesy of ACS publications.

4.1. Water temperature

Ozone's solubility in water at 20 °C is 12.07 mg/L. Based on Henry's law, it is well-know that the solubility of ozone decreases with increasing temperature. It is also known that ozone decomposes in water to yield hydroxyl (OH$^\bullet$) radicals. However, the reaction rate of O_3 decomposition is much faster at higher water temperature. A direct benefit of this dominance of reaction rate over mass transfer rate can be observed in the work of Ikeura, Kobayashi, et al. (2013), where degradation of fenitrothion increased with temperature rise from 15 to 30 °C.

4.2. Humidity in gas phase

The stability of ozone in air exceeds that in water; however, both stabilities are within the order of minutes (Chen, et al., 2013). The generation of ozone within the source and the recombination rates of gas phase ozone, both are affected by the humidity levels (Misra, Ziuzina, Cullen, & Keener, 2013; Moiseev, et al., 2014). There have been no reported studies looking into the effects of humidity levels on efficacy of gas phase ozone fumigation against pesticide residues or other chemicals in general.

4.3. Produce Geometry

The effectiveness of pesticide degradation with ozone washing also depends on the geometrical features of the produce. For example, it has been shown that ozone microbubbles are more effective in dissipating fenitrothion concentration on lettuce than cherry tomatoes under identical conditions (Ikeura, Kobayashi, et al., 2013). This has been explained on the basis of the thick pericarp of cherry

Preprint submitted to Trends in Food Science & Technology

tomatoes which pose difficulty for the O_3 and hydroxyl radicals to penetrate and reach the internal tissues (sarcocarp).

4.4. Matrix pH

The efficiency of not only ozone, but any approach in degrading pesticides is dependent on the pH of the matrix being treated. This is because the ion concentrations regulate the shift in equilibrium. For example, alkaline conditions are suitable for degrading malathion and dichlorvos with ozone, whereas acidic conditions are suitable for cypermethrin (Lin, et al., 2012).

4.5. Bubble size

For dissolved ozone applications, the size of ozone bubbles dictates their residence time in the reactor and therefore, the mass transfer rate. Microbubbles technology (bubble diameter, 10-50 μm) has been explored for ozone bubbling into wash water for fruits and vegetables and rapid pesticide degradation has been recorded (Agarwal, Ng, & Liu, 2011; Ikeura, Hamasaki, et al., 2013; Ikeura, et al., 2011a, 2011b). The relatively smaller sizes of microbubbles boosts the mass transfer rates, which reflects in their greater efficacy compared to bubbling with standard bubble spargers.

While ozone microbubbling has been studied for applications in pesticide breakdown during fruit and vegetable washing, the use of nano-bubbles for ozone remains unexplored. The potential of nano-bubbles is successfully being exploited in other areas, including water treatment (Agarwal, et al., 2011). It is anticipated that the extremely high mass transfer efficiency of nanobubbles could dramatically enhance the effects of ozone, not only for pesticide breakdown, but also antimicrobial action.

5. Ultrasound

Ultrasound is a form of energy generated by sound waves (which are mechanical in nature) of frequencies that are too high to be detected by human ear, i.e. above 16 kHz (Ghafoor, Misra, Mahadevan, & Tiwari, 2014). When ultrasound propagates through any medium, it induces a series of compression and rarefaction in the molecules of the medium. Such alternative pressure changes cause formation of bubbles in a liquid medium. This phenomenon of the creation, expansion, and implosive collapse of microbubbles in ultrasonically irradiated liquids is known as "acoustic cavitation". The applications of ultrasound in food processing were recently reviewed (Rastogi, 2011). Most of the effects of power ultrasound (hereafter referred to as ultrasound only) in sonochemistry has been attributed to (transient) cavitation phenomenon.

The chemical effects of ultrasound have been studied extensively within the last century. Under the extreme temperature and pressure conditions at cavitation interface, highly reactive radicals are generated. For example, if water is the medium, H· and OH· radicals are generated via the dissociation

Preprint submitted to Trends in Food Science & Technology

of water into hydroxide ion ($H_2O \rightarrow OH^- + H^+$) (see **Figure 6**). Both stable cavitation and an increase in the number of active bubbles can be expected to increase the amount of hydroxyl radicals generated with an increase in the ultrasound frequency. These primary radicals induce a wide variety of chemical reactions in the bulk liquid/aqueous media and fruit juices, rendering the ability to rapidly dissipate pesticide residues.

While the ultrasonic degradation of pesticides and pollutants in water or waste water has received much attention within last few years, the exploitation of ultrasound technology for pesticide breakdown has remained under-researched. Literature reveals a series of important studies carried out by Zhang and co-workers investigating the effect of ultrasound on pesticides in fruit juices (Zhang, Xiao, et al., 2010; Zhang, Zhang, et al., 2010; Zhang, Zhang, Chen, Zhang, & Hu, 2012). This group reported significant reductions in concentrations of malathion, chloropyrifos, diaznion and phorate in apple juice following ultrasound treatments. All the studies have indicated the ultrasound power and treatment time to be the most significant factors influencing the degradation of pesticides. In addition the extent of breakdown is dependent on the chemical structure of the pesticide. For example, chlorpyrifos is much more labile to ultrasound treatment than malathion (Zhang, Xiao, et al., 2010). The breakdown products of malathion and chlorpyrifos have been confirmed to be malaoxon and chlorpyrifos oxon respectively, which form by oxidative desulfuration caused by hydroxyl radicals formed in the aqueous media (see **Figure 2**). While a similar breakdown mechanism has also been proposed for phorate (**Figure 2**) (Zhang, Zhang, et al., 2012), the degradation pathway could be much more complex as with ultrasonic breakdown of diaznion, involving hydrolysis of the ester moiety, oxidation, hydroxylation, dehydration, and decarboxylation (Zhang, Zhang, et al., 2010).
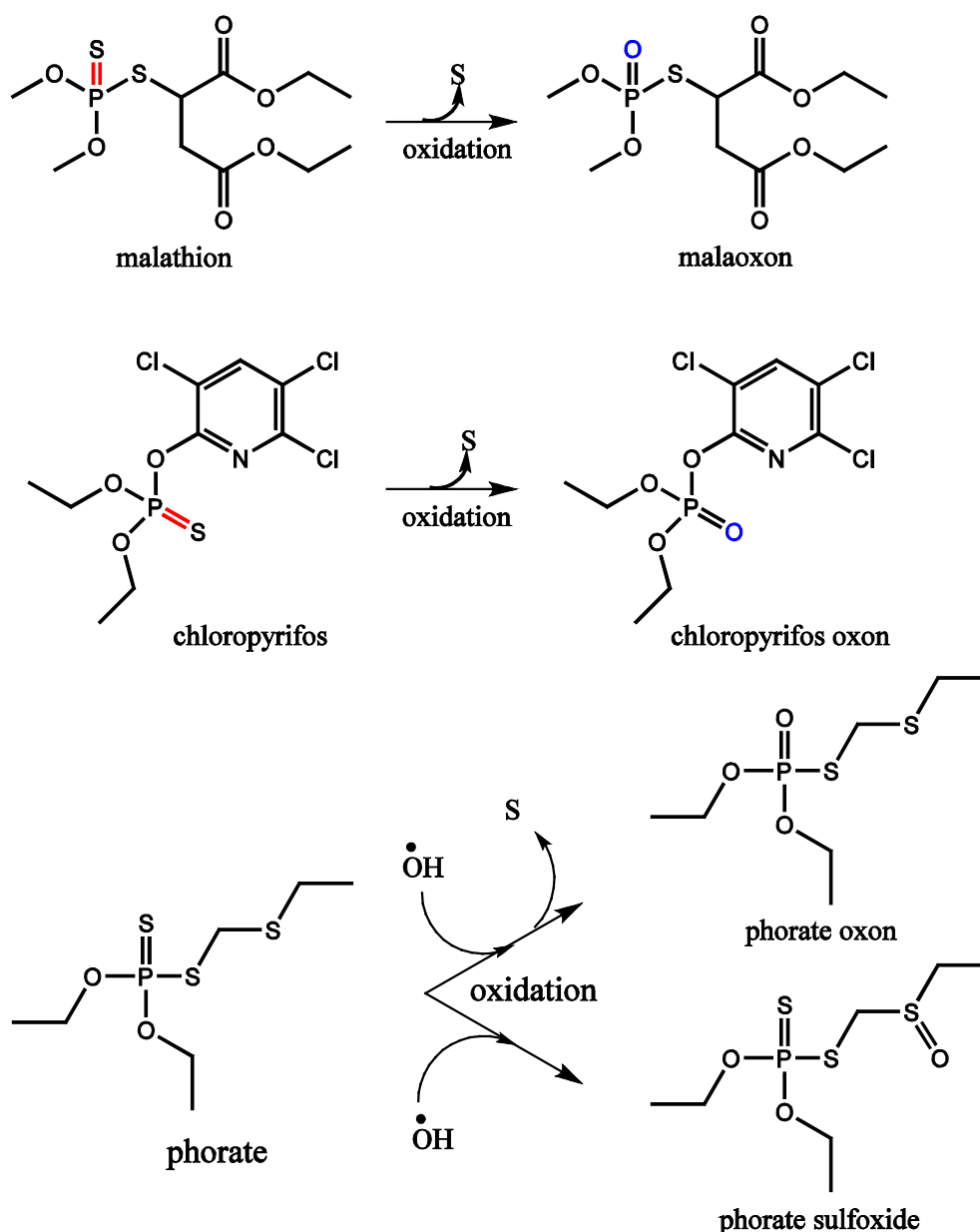
Figure 2 Degradation pathway of malathion, chloropyrifos and phorate in apple juice proposed by Zhang, Xiao, et al. (2010) and Zhang, Zhang, et al. (2012). The mass-spectrum of the end products was used for confirmation. (Courtesy of Elsevier publications)

The ability of ultrasound to cause cavitation depends on ultrasound characteristics (e.g. frequency and intensity), product properties (e.g. viscosity and surface tension) and ambient conditions (e.g. temperature and pressure). Therefore, extrinsic control parameters such as frequency, amplitude, ultrasonic intensity, treatment time, and temperature strongly influence the chemical effects of ultrasound. By suitably interplaying with these factors, optimised conditions for favourable and rapid breakdown of pesticides with minimal adverse changes in food quality can be achieved. A summary of selected studies reporting the degradation of pesticides in fruit juice and aqueous media by ultrasound application, along with the process parameters explored, is provided in **Table 2**.

Preprint submitted to Trends in Food Science & Technology

Table 2 Synopsis of studies on degradation of pesticide residues using ultrasound.

Pesticide	Matrix	Process	Analytical Method	Salient Results	Reference
malathion and chlorpyrifos	Apple juice (pH 3.86)	Ultrasonic probe (25 kHz) with 6.0 mm horn tip diameter dipped 10 mm below liquid surface; Treatment time: 15, 30, 45, 60, 75, 90, 105, 120 min; Treatment power: 100, 300, 500 W; Temperature: 15 °C.	Acetonitrile-Acetone extraction, followed by GC-MS quantification	Maximum degradation for malathion (41.7 %) and chlorpyrifos (82.0 %) were achieved at 500 W ultrasonication for 120 min; First order reaction kinetics was found adequate.	Zhang, Xiao, et al. (2010)
Diazinon	Apple juice (pH 3.86)	Ultrasonic probe (25 kHz) with 6.0 mm horn tip diameter dipped 10 mm below liquid surface; Treatment time: 15, 30, 45, 60, 75, 90, 105, 120 min; Treatment power: 100, 300, 500 W; Temperature: 15±2 °C.	Acetonitrile-Acetone extraction, followed by GC-MS quantification	Degradation efficacy increased with treatment time as well as power; Degradation followed first-order kinetics and involved hydrolysis of the ester moiety, oxidation, hydroxylation, dehydration, and decarboxylation	Zhang, Zhang, et al. (2010)
Phorate	Apple juice	Ultrasonic probe (25 kHz) with 6.0 mm horn tip diameter dipped 10 mm below liquid surface; Treatment time: 15, 30, 45, 60, 75, 90, 105, 120 min; Treatment power: 100, 300, 500 W; Temperature: 15±1 °C.	Acetonitrile-Acetone extraction, followed by GC-MS quantification	Higher sonication power and treatment times were reported effective. Phorate-oxon and phorate sulfoxide were identified as the degradation products and degradation followed first-order kinetics.	Zhang, Zhang, et al. (2012)
Carbofuran	Aqueous solution	Near-field acoustical processor (16 and 20 kHz) with a total power input of 1800 W and a power-to-area ratio of 1.22 W/cm^2; Sonoactive volumes: 1089, 426, and 324 mL. Solutions saturated with $Ar+O_2$ mixture	Filtration followed by HPLC analysis	Carbofuran decomposition followed pseudo first-order kinetics. Degradation efficacy increased with increasing power densities and decreasing initial concentration.	Hua and Pfalzer-Thompson (2001)
Dichlorvos	Aqueous solution	Pulsed sonication at 500 kHz in jacketed reactor; input powers ranged from 86 to 161 W; Temperature: 20±6 °C; Solutions saturated with $Ar/O_2/Ar+O_2$ mixture	Extraction with Hexane, followed by GC-ECD estimation	Degradation increased with applied power and treatment time, and followed first-order kinetics; $Ar+O_2$ mixture was found most efficient	Schramm and Hua (2001)
methyl parathion	Aqueous solution	Ultrasonic horn (20 kHz, 270 W, 1 cm below liquid surface) and ultrasonic bath (20 kHz, 230 W).; pH: 2.5-9.3, temperature: 30 °C; initial concentration = 20 ppm	Centrifugation followed by HPLC quantitation	Degradation efficacy was higher at acidic pH, followed first-order kinetics; ultrasonic probe slightly more efficient than bath; combination with Fenton reagent	Shriwas and Gogate (2011)

				increased the efficacy.	
Parathion	Aqueous solution	Sonication in open cylindral stainless steel reaction vessel with bonded transducers at 200, 400, 600 and 800 kHz frequency; Temperature: 25.0 ± 1.0 °C	Solid-Phase extraction (SPE) in methanol, dichloromethane, followed by GC-MS quantification	Degradation rate of parathion decreased with increasing initial concentration and decreasing power; optimal frequency was 600 kHz; degradation followed first-order kinetics	Yao, Gao, Li, Li, and Xu (2010)
chlorpyrifos and diazinon	Aqueous solution	Ultrasonic horn @ 20 kHz frequency; Power: 300, 600, 900 W; Treatment times: 1-120 minute; pH: 5, 6, 7, and 8; Temperature: 15, 25, 35 °C	Dichloromethane, Acetone extraction followed by GC-FPD quantification and GC-MS identification	Degradation efficacy increased with sonication power and time; highest efficacy was obtained at pH 7.0 and 25 °C; toxicity decreased for diazinon after ultrasonication, but increased for chlorpyrifos.	Zhang, et al. (2011)

In spite of the promising results with ultrasound, in most of the cases no decisive success in the food industry has been achieved to date (Deora, et al., 2013). One drawback of ultrasound technology is the long treatment times required in the order of 1 to 2 hour to achieve significant reductions in pesticide concentrations (Zhang, Zhang, et al., 2012), which invariably will result in significant loss of bioactive components and chemical quality of fruit juices. A possible solution for decreasing the processing times without losing the effectiveness could involve coupling different technologies. Commercial standard ultrasonic equipment are being developed at great pace and any novel process for the application of ultasonics in industry is not possible without equipment manufacturers willing to customize and develop new designs according to the requirements of food industry.

6. UV light

The ultraviolet spectrum of the electromagnetic radiation can be distinguished between UV-A (380 - 315 nm), UV-B (315 - 280 nm), UV-C (280 - 200 nm), vacuum-UV (VUV) (200 - 100 nm), and extreme UV (100 - 1 nm). UV radiation for processing applications is generally obtained from low-pressure mercury vapour lamps (185 and 254 nm) or xenon excimer radiators (emitting at 172 nm). The application of ultraviolet light in food processing has been reviewed in the past by several authors (Falguera, Pagán, Garza, Garvín, & Ibarz, 2011; Koutchma, Forney, & Moraru, 2010). The electronic excitation of water in the ultraviolet spectral region between 190 to 120 nm induces its homolysis, leading to the production of a large amount of hydroxyl radicals. The use of intense UV light can promote the degradation of some pesticides by direct photolysis due to their potential to absorb light.

In one of the earliest studies, Li and Bradley (1968) demonstrated the potential of high-intensity ultraviolet light (220-330 nm) from a carbon arc lamp in degrading the organochlorine insecticides in

whole fluid milk and butter oil. A 96% reduction in the concentration of methoxychlor was observed after a single exposure and the vitamins (A and D) and β-carotene were well-retained under these conditions. Cin and Kroger (1982) reported that ultraviolet irradiation led to significant reductions in mirex concentration in the muscle of brown trout following exposure to ultraviolet light. However, the treatment times required were quite long with 45% reduction after 72 h of exposure. It is only about 27 years later when Nieto, Hodaifa, and Casanova (2009) have attempted to develop a simple UV immersion system (200-280 nm, power = 150 W) to reduce the amount of pesticides present in virgin olive oil. Upon treatment of olive oil spiked with a pesticide cocktail the concentrations reduced by levels of 7 to 80%, depending on the treatment time and temperature (evaluated at 15, 20, 25, and 30 °C). In addition, the quality parameters evaluated were found to be insignificantly affected following the treatments. While these results opened the possibility of using ultraviolet light as an effective and low-cost process for pesticide dissipation in olive oil, no further progress has been reported in this regard. Brun, Merlet, Croue, and Doré (1993) investigated the aqueous phototransformations of atrazine by UV (254 nm) and polychromatic light. The authors proposed a complex mechanism, including oxidation, dealkylation, and hydrolysis, and also suggested a significant involvement of radicals in these processes. For the mechanism of photodegradation of pesticides and the associated reaction pathways, we redirect to the review by Burrows, Canle L, Santaballa, and Steenken (2002).

In general, the effectiveness of ultraviolet light has been found to be lower when compared with other AOPs such as ultrasound and ozone, even in liquid media. The effectiveness of ultraviolet light to degrade pesticides will be far less in turbid environments than in clear solutions (Autin, et al., 2013). This appears to be an important reason for far less popularity of UV treatment for pesticide dissipation among researchers. Nevertheless, UV light is far more effective in degrading pesticides in comparison to gamma-irradiation. To quote an example, it has been reported that exposure of contaminated apple juice to ultraviolet light led to complete degradation of organochlorine pesticide (UV-C, 30 min exposure), whereas only 30% decrease in concentration was recorded with gamma-radiation (25 kGray) (Herzallah, 2009). Despite the anomalies between results, UV light can be easily coupled with ultrasound, ozone, catalysts (e.g. TiO_2) or hydrogen peroxide to obtain synergistic effects and has been widely explored for water treatment (Abramovic, Banic, & Sojic, 2010; Tizaoui, Mezughi, & Bickley, 2011) and only recently for dissipation of pesticides on tea leaves (Lin, et al., 2012).

7. Gamma Irradiation

Gamma irradiation has been proven to be safe and effective for elimination of food-borne pathogens and pests by World Health Organization and U.S. Food and Drug Administration, and is in use for improving food safety for fresh foods and dried raw materials (Wen, et al., 2010). Radiation from cobalt-60 source is the most commonly employed for successful pesticide degradation studies. In general, high-energy radiation from any system generates highly reactive intermediates (hydrated

electrons, OH• radicals and H atoms in water) in aqueous solutions. As per the International Atomic Energy Agency (IAEA), irradiation doses of up to 1.5 or 2.0 kGy are deemed to be safe for foods.

Gamma irradiation was reported to cause significant reductions in mirex levels in brown trout fish muscle, with up to 37.5% breakdown for a dose of 5 Mrad (Cin & Kroger, 1982). The application of gamma-irradiation for degradation of commonly encountered pentachloronitrobenzene (PCNB) pesticide in American ginseng (*Panax quinquefolius*) was first demonstrated by Wen, et al. (2010). This group reported ca. 80% degradation of PCNB (initial concentration of 3.7 ppm) with a total radiation dose of 10 kGy. Up to 30% degradation of organochlorine pesticides in apple juice after a dose of 25 kGy, while insignificant effects at 5 kGy dose has been reported (Herzallah, 2009). Basfar, Mohamed, and Al-Saqer (2012) investigated the effects of irradiation on pesticide residues in several fruits and vegetables. The Irradiation at 1 kGy of potatoes and dates resulted in 18% and 44.4% removal of the initial 0.05 ppm and 0.1 ppm concentrations of pirimiphos-methyl residues, respectively. In a recent study, Chowdhury, et al. (2014) found that irradiation at 1.0 kGy dose reduced the levels of chlorpyrifos in cucumber, diazinon in capsicum and phosphamidon in tomato by 80-91%, 85-90%, and 90-95% respectively.

The irradiation induced breakdown of pesticides in fruits and vegetables was reported by Basfar, et al. (2012), who observed that irradiation at 1 kGy of potatoes and dates results in 18% and 44.4% removal of the initial 0.05 ppm and 0.1 ppm concentrations of pirimiphos-methyl residues, respectively. Surprisingly, at 7 kGy malathion, pirimiphos-methyl and cypermethrin (starting at 8 ppm, 1 ppm and 2 ppm respectively) are reduced by only 3.83%, 19.1% and 2.6% respectively in grapes.

Gamma radiolysis was shown to cause 90% destruction of diazinon in water when absorbed doses range between 1.5 to 5.6 kGy (Basfar, Mohamed, Al-Abduly, Al-Kuraiji, & Al-Shahrani, 2007). Zhang, et al. (2008) also reported a complete removal of diuron in aqueous solution at 18.5 mg/L initial concentration, with a radiation dose of 1.0 kGy. The duration of irradiation (total dose) is important to ensure complete oxidation of the intermediate diazoxon into IMP (2-isopropyl-6-methyl-pyrimidine-4-ol), considering that the former is more toxic than diazinon itself. The higher toxicity of transient intermediates in irradiation induced degradation pathway for herbicides 2,4-D and dicamba were also confirmed using microtox tests (Drzewicz, et al., 2004). A preferential reactivity of the radiation products with the pesticides is also reported. Mohamed, Basfar, Al-Kahtani, and Al-Hamad (2009) reported a rapid degradation of malathion in distilled water at low absorbed doses (requires 1.77 kGy dose for 90% removal) compared to lindane (requires 28.79 kGy dose for 90% removal).

Among the AOPs, irradiation is different as both oxidizing as well as reducing reactive species (i.e., hydroxyl radicals and aqueous electrons, respectively) are produced simultaneously during irradiation. Upon irradiation in aqueous media, endosulfan is attacked by radiolytically generated hydroxyl

Preprint submitted to Trends in Food Science & Technology

radical at the sulfoxide site via electron transfer mechanism (oxidative pathway), followed by hydrolysis and subsequent beta-elimination of the intermediate to yield endosulfan ether. The endosulfan ether is further transformed into endosulfan lactone, chlorendic acid and through further oxidation into acetate ions (Shah, Khan, Nawaz, & Khan, 2014) (see **Figure 3** for the reaction scheme). The aqueous electron plays an important role in reductive pathways where it acts at the chlorine attachment site to yield chloride ions and intermediate radicals (Shah, et al., 2013; Shah, et al., 2014). These intermediates are driven into reactions similar to the oxidative pathway, yielding endosulfan ether.
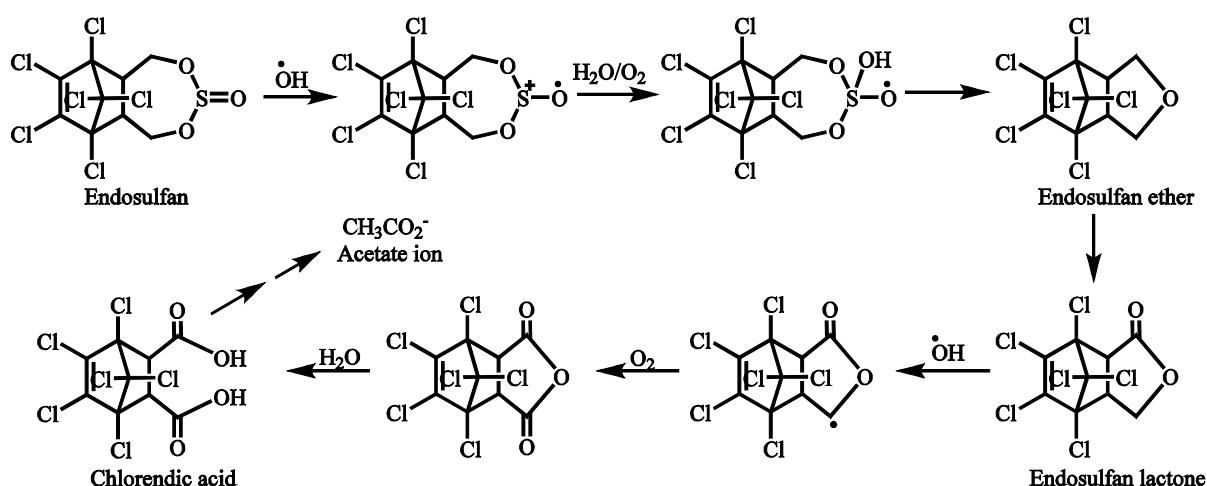

Figure 3 Degradation mechanism of endosulfan by irradiation, which dominantly generates hydroxyl radical. Based on Shah, et al. (2014) and Shah, et al. (2013). Courtesy of Elsevier publications.

As a general conclusion, the decontamination of pesticide residues is often reported to be much greater in irradiated aqueous solutions than in irradiated food matrices (Basfar, et al., 2012; Wen, et al., 2010). In addition, the efficacy of breakdown in foods is dependent on the nature of food, the radiation dose, the type of pesticide and the initial concentration.

8. Non-thermal Plasma (NTP)

The term 'plasma' refers to a partially or wholly ionized gas composed essentially of photons, ions and free electrons as well as atoms in their fundamental or excited states possessing a net neutral charge (Misra, Tiwari, Raghavarao, & Cullen, 2011). Two classes of plasma, namely thermal and NTP can be distinguished on the basis of the thermodynamic temperature equilibrium between the electrons and relatively heavy particles. NTP is characterized by an electron temperature (T_e) much above that of the macroscopic gas temperature (T_g) ($T_e \gg T_g$) and consequently do not possess a local thermodynamic equilibrium (Misra, Keener, Bourke, Mosnier, & Cullen, 2014). NTP can be generated by an electric discharge in a gas at ambient or low pressure. Typical approaches for plasma generation at atmospheric pressure include the corona discharge, dielectric barrier discharges (DBD),

radio frequency plasma (RFP) and the gliding arc discharge. Plasma technology has been explored only recently for the decontamination of foods, food processing surfaces and water treatment. The fundamentals and application of NTP for inactivation of food-borne pathogens were recently reviewed (Misra, Tiwari, et al., 2011).

The degradation of dichlorvos and omethoate (organophosphorus) pesticides sprayed onto maize samples when treated with an inductively coupled radio-frequency NTP source operating in oxygen was studied by Bai, Chen, Mu, Zhang, and Li (2009). It was found that at 120 W of discharge power, 120 s of treatment time, and 40 cm^3/min of O_2 flux, a complete degradation of the pesticides occurs. By employing a radical scavenger (t-butanol), this group confirmed the degradation pathway to be free radical mediated. Most of the intermediates identified in this study were confirmed to be far less toxic than the original pesticides. In an earlier study, Kim, Kim, and Kang (2007) also reported the decomposition of parathion and paraoxon deposited on a solid surface with an atmospheric pressure, radio-frequency plasma generated in Ar and Ar/O_2 mixture. The atomic oxygen and excited $OH^\bullet$ species generated by the plasma were suggested to be the key species responsible for oxidation of parathion and paraoxon. A complete detoxification of the pesticides was also confirmed by using a biological assay (viz. the *Drosophila melanogaster* culture test). It should be noted that when Ar is used as the carrier gas in plasma diffusing into an aqueous liquid media, $OH^\bullet$ radicals can be generated by dissociative excitation of water vapour with metastable Ar as follows (Shen, et al., 2014):

$$Ar^* + H_2O \rightarrow Ar + OH^\bullet + H^\bullet$$
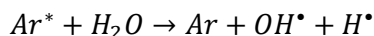
Recently, Bai, Chen, Yang, Guo, and Zhang (2010) demonstrated the successful degradation of dichlorvos pesticides coated on glass slides using the same inductively coupled plasma (ICP) source. However, it was observed that an increase in applied power to plasma had insignificant effect on the degradation of dichlorovos. Similar results were obtained by Misra, Pankaj, et al. (2014) during in-package gas phase plasma treatment of strawberries loaded with azoxystrobin, cyprodinil, fludioxonil and pyriproxyfen. The degradation kinetics indicated that the rate of pesticide dissipation decreased with increase in treatment time. This effect was ascribed to the kinetics of plasma chemistry in air, where excited nitrogen species are favoured over oxygen species for extended time scales (Kossyi, Kostinsky, Matveyev, & Silakov, 1992). Despite their short life-time, the excited nitrogen species are capable of shielding the action of ozone by promoting local acidic environments, even during the post-discharge period. Misra, Pankaj, et al. (2014) identified the end product of degradation of fludioxonil using mass-spectrometry and proposed a reaction pathway as shown in **Figure 4**, considering the dominance of ozone during post-discharge storage in the headspace gas of the package containing strawberries. The end product of the degradation pathway, a carboxylic acid, possessed low toxicity and low risk (EFSA, 2007).
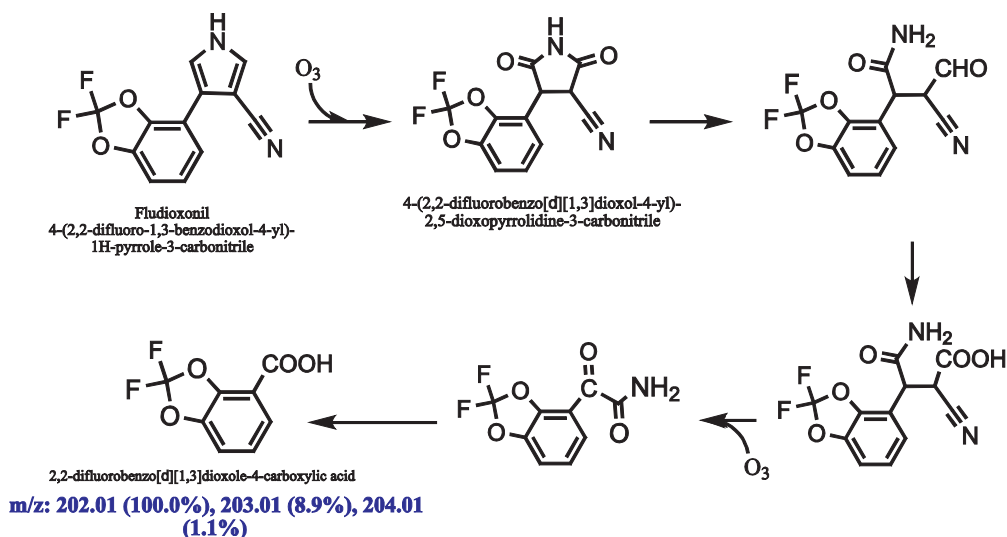
Figure 4 Mechanism of degradation of fludioxonil during in-package, gas phase, non-thermal plasma treatment of pesticides. Adapted from Misra, Pankaj, et al. (2014); Courtesy of Elsevier publications.

The degradation of malathion (sprayed on a filter paper) following exposure to an atmospheric pressure plasma jet operating in He/O_2 has also been demonstrated (Zhu, Wang, Xi, & Pu, 2010). The various possible pathways of degradation are enlisted in **Figure 5**, from which it becomes clear that the P=S bond of malathion is oxidised by the energetic oxygen species of plasma to P=O, thereby resulting in formation of diethyl 2-(dimethoxyphosphorylthio)maleate (malaoxon). Further degradation follows from attack at P-S and S-C bonding.
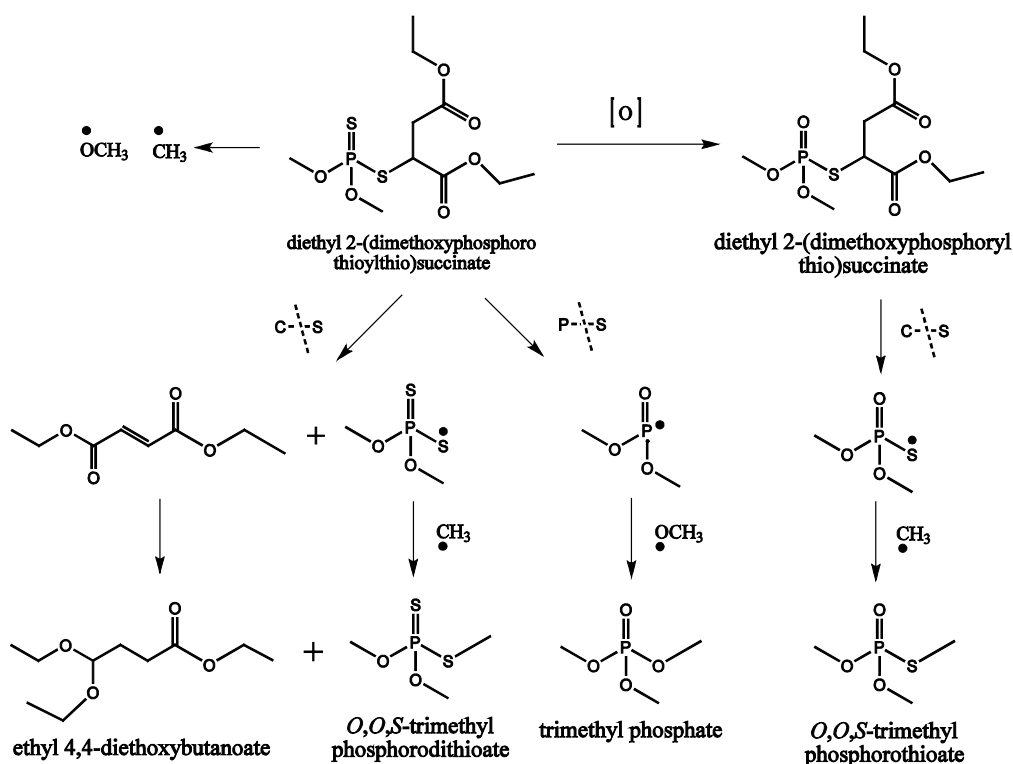

Figure 5 Degradation mechanism of malathion in atmospheric pressure radio-frequency plasma jet. Adapted from Zhu, et al. (2010) by courtesy of Springer Science.

Preprint submitted to Trends in Food Science & Technology

While NTP has been shown to degrade a variety of conventional and contemporary pesticides, independent studies reveal that the efficacy of NTP can vary depending on the complexity of the chemical makeup and structure of the pesticide. This is evident from the fact that insignificant differences in residual pesticide concentration relative to control was observed for boscalid, pyrimethanil and iprodione in plasma treated strawberries (Misra, Pankaj, Bourke, & Cullen, 2013). In addition, plasma chemistry can be very complex with a large number of different constituent species at any given point of time. For example, in air plasma the chemistry is believed to include more than 75 species and almost 500 reactions (Gaens & Bogaerts, 2013). Typical examples of relatively long-lived active species in humid air plasma include ozone, atomic oxygen, peroxide, superoxide, excited molecular nitrogen and several oxides of nitrogen. Thus, without surprise, the myriad of active chemical species in NTP impart it the capability to rapidly dissipate pesticide residues through multiple simultaneous reaction pathways, even in gas phase. As an example, while nitrogen species in plasma can shield the ozone formation, the nitrate radicals themselves have been shown to rapidly degrade the N,N-dialkyl substituted pyrimidine pesticides viz. pirimiphos-methyl (PMM) and pirimicarb (PM) (Wang, et al., 2012).

Table 3 Salient results of studies concerning non-thermal plasma assisted degradation of pesticides.

Pesticide	Matrix	Process	Analytical Method	Salient Results	Reference
paraoxon and parathion	Glass slide	Scanning atmospheric RF plasma in Ar gas @ 4000 cm^3 flow rate; 13.56 MHz RF source, 150 - 250 W power; O_2 as reactive gas @ 20 cm^3 flow rate	Polarization-Modulation Reflection-Absorption Infrared Spectroscopy (PM-RAIRS)	Excited gaseous species identified as atomic oxygen, OH radical, and excited nitrogen molecule; paraoxon and parathion were oxidised; plasma-induced decomposition was faster and efficient than UV/ozone process.	Kim, et al. (2007)
dichlorvos (DDVP) and omethoate	Maize	Inductively coupled oxygen plasma reactor operating using 13.56 MHz, 500 W RF power source. Treatment times: 30, 60, 90, and 120 s at discharge power levels of 30, 60, 90, and 120 W with different O_2 flux	Extraction with acetone, followed by GC-MS analysis	Treatment in discharge zone was more effective (95% reduction) than afterglow or remote regions. A power of 120 W for 120 s was optimal for effective reduction.	Bai, et al. (2009)
dichlorvos (DDVP)	Pesticide sample spin-coated on to glass slide	Inductively coupled oxygen plasma reactor operating using 13.56 MHz, 500 W RF power source. Treatment times: 30, 60, 90, and 120 s at discharge power levels of 30, 60, 90, and 120 W	Extraction with acetone, followed by GC-MS analysis	Treatment is more effective at lower DDV concentration. Optimum conditions: plasma treatment time of 120 s; discharge power of 120 W, and O_2 flow rate at 40 cm^3	Bai, et al. (2010)

Preprint submitted to Trends in Food Science & Technology

		with different O_2 flux. Samples placed at 0, 20, 40, 60 and 80 cm from centre of induction coil		min^{-1}; sample placement in discharge zone.	
Malathion	5 µl on a filter paper (2.17 mg/cm^2)	Capacitively coupled atmospheric pressure radio-frequency (RF) plasma jet in a mixture of helium and oxygen; powered at 13.65 MHz frequency	Dichloromethane extraction, followed by GC-MS analysis	Degradation efficiency increased with the exposure time and applied RF power. The S-C and the P-S bonds were broken, oxidation of P=S bond also occurred.	Zhu, et al. (2010)
paraoxon, in a 10% (v/v) methanol solution	Apple	Dielectric barrier discharge (DBD) in 99.9% pure air, powered using RF AC source; treatments carried out in a commercial refrigerator	Extraction using methanol, followed by HPLC-UV analysis	An average reduction of 95.9% was recorded; The degradation ratio is dependent on initial concentration.	Heo, et al. (2013)
azoxystrobin, cyprodinil, fludioxonil and pyriproxyfen	Strawberry	In-package plasma from a DBD at 60, 70 and 80 kV for 0-5 min duration followed by 24 h storage	mini-Luke extraction using acetone, dichloromethane and petroleum ether mixture (1:1:1) followed by GC-MS/MS	Voltage and time dependent degradation; levels of azoxystrobin, cyprodinil, fludioxonil and pyriproxyfen decreased by a maximum of 69%, 45%, 71 and 46% respectively after 5 minute at 80 kV.	Misra, Pankaj, et al. (2014)
atrazine, chlorfenvinfos, lindane	Aqueous media	Planar DBD operating at 20 kV potential difference, 100 kHz frequency across a 16 mm gap in Helium; treatment times (0 s, 10 s, 30 s, 2 min, 5 min, 15 min); Sample temperature < 40 °C	Solid-phase microextraction coupled with GC-NPD for atrazine, chlorfenvinfos and GC-ECD for lindane	Removal efficiency was higher than conventional AOPs and followed first-order kinetics; the degradation by-products did not disappear completely within the treatment time (15 min).	Hijosa-Valsero, Molina, Schikora, Muller, and Bayona (2013)

A summary of the important studies reporting the degradation of pesticides using NTP is provided in **Table 3**. Clearly, the process variables for optimisation of NTP effects vary with the type of set-up employed and include power applied, operating frequency, electrode contact area, discharge gap, distance from plasma source, treatment time, discharge gas type, gas pressure and gas flow rate, besides the packaging material used (Kelly & Turner, 2014; Misra, Moiseev, et al., 2014; Pankaj, Bueno-Ferrer, Misra, Milosavljević, et al., 2014; Pankaj, Bueno-Ferrer, Misra, O'Neill, et al., 2014). Therefore, plasma processes, despite their versatility and robustness pose a great challenge in terms of controlling the reaction chemistry for optimal effects, especially due to the high degree of freedom of gas molecules and the involvement of several process variables. Various approaches to tackle this challenge are under active research in plasma physics and engineering domains. Furthermore, when

Preprint submitted to Trends in Food Science & Technology

noble gases are involved, the cost of the process could turn out to be very high. It has been shown that for the correct comparison of energy efficiency of various plasma sources, it is necessary to specify not only the discharge power but also the degree of pesticide breakdown, its initial concentration, initial pH value, and solution volume (Bobkova & Rybkin, 2015). The most promising aspect of NTP is that it has been found to result in insignificant changes in food quality (Misra, Keener, et al., 2014; Misra, Patil, et al., 2014).

9. Combined approaches

Several studies have aimed at exploiting the benefits of combining two or more non-thermal technologies based on advanced oxidation processes to achieve enhanced degradation effects for several applications, including not only pesticides, but also pollutants and microbiological decontamination. The principal factor governing the improved efficacy and synergistic effects of combining two or more approaches lies in the modulation of the reaction chemistry. A summary of the reactions occurring in aqueous media for ozone, ultrasound, ozone with ultrasound, and ozone with UV light are provided in **Figure 6**. Apparently, it becomes clear that the reaction chemistries presented are different avatars of the basic hydroxyl radical production, which is the most powerful oxidant known to occur in water.
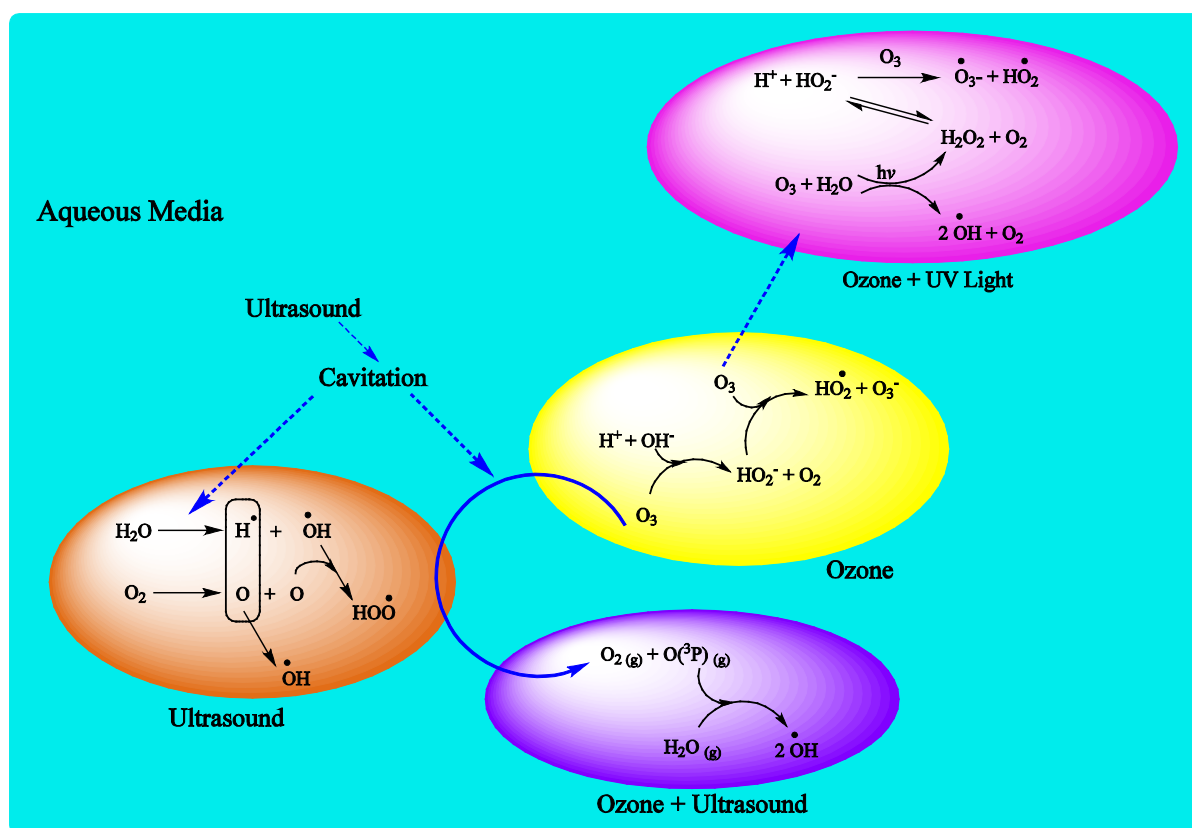

Figure 6 Principal reactions governing non-thermal technologies based on advanced oxidation processes (AOPs), either alone or in combination, in aqueous liquid medium. (Colour online)

Preprint submitted to Trends in Food Science & Technology

In most cases combining two or more approaches allows enhanced production of one or more active species. In general, the concentration of hydroxyl radicals increases when ozone is combined with ultrasound or UV light resulting in enhanced effects. For example, Lafi and Al-Qodah (2006) observed that the use of ozone combined with UV radiation enhances pesticides degradation in aqueous solutions (see Figure 7). However, it should be noted that the desired reactions in liquid media largely rely on shifting the equilibrium relations, which requires maintenance of the right pH conditions. In most cases, acidic pH favours the formation of hydroxyl radicals.
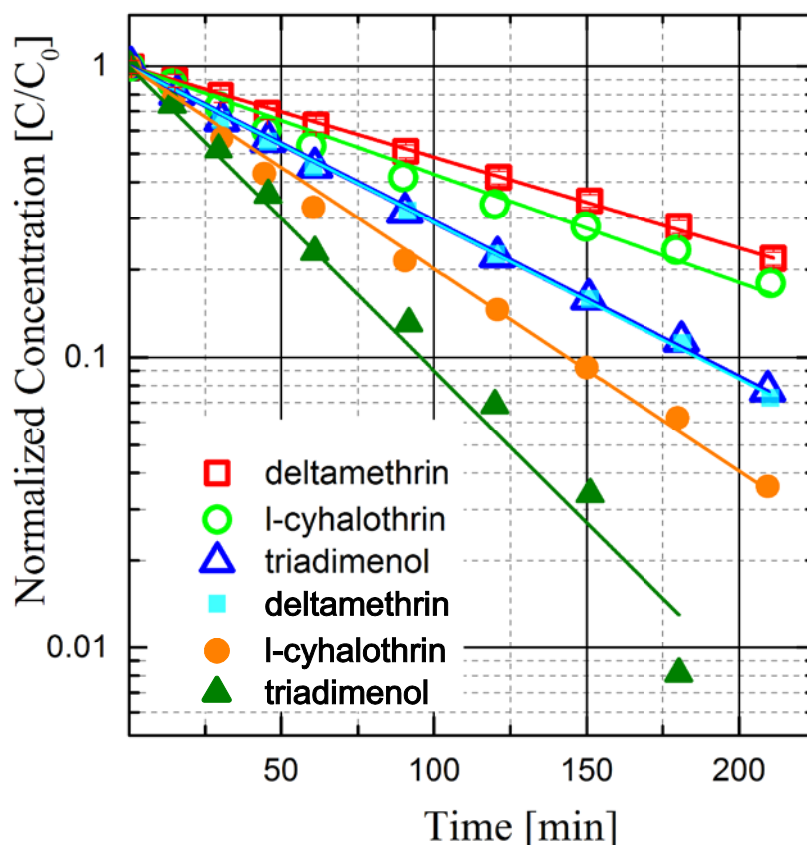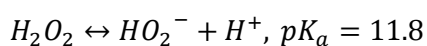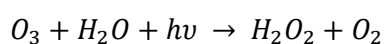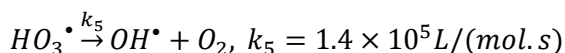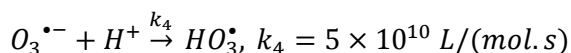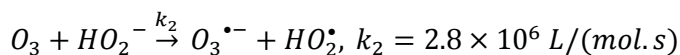

Figure 7 The variation of the normalized concentration of three pesticides using Ozone oxidation (open symbols) and Ozone/UV system; For both cases, C_0 = 100 mg/L, T = 25 °C, pH=7 (closed symbols). Data adapted from Lafi and Al-Qodah (2006) by courtesy of Elsevier. (Colour online)

An enhanced degradation of 4-chlorophenol (used as a pesticide and herbicide) in presence of combined ozone and UV radiation was recently confirmed (Ebrahimi, Mohammadi, Sharifi, Asgari, & Attar, 2013). The enhanced pesticide dissipation effect of ozone in presence of UV radiation (also known as photocatalytic ozononation) can be attributed to the greater production of OH• radicals following a series of chemical reactions, which are summarised as follows:

$$O_3 + H_2O + hv \rightarrow H_2O_2 + O_2$$

$$H_2O_2 \leftrightarrow HO_2^- + H^+, pK_a = 11.8$$

Preprint submitted to Trends in Food Science & Technology

$$O_3 + HO_2^- \xrightarrow{k_2} O_3^{\bullet-} + HO_2^\bullet, \; k_2 = 2.8 \times 10^6 \; L/(mol.s)$$

$$O_3^{\bullet-} + H^+ \xrightarrow{k_4} HO_3^\bullet, \; k_4 = 5 \times 10^{10} \; L/(mol.s)$$

$$HO_3^\bullet \xrightarrow{k_5} OH^\bullet + O_2, \; k_5 = 1.4 \times 10^5 L/(mol.s)$$

It may be noted that ozone when used in combination with hydrogen peroxide also generates high concentration of OH$^\bullet$ radicals.

Another approach, not so common with fruit juices or liquid foods (for obvious problems of oxidation) but often employed in water treatment is the addition of hydrogen peroxide (H_2O_2) or a catalyst to enhance the reaction rates. This approach is especially advantageous when UV irradiation is selected as the primary mode, because direct photolysis using UV is often insignificant for rapid pesticide dissipation (e.g. parathion and chlorpyrifos, as in Wu and Linden (2010)) due to their low quantum yields and molar absorption coefficients. The addition of H_2O_2 can significantly increase the reaction rates by formation of hydroxyl radicals through the photolysis of H_2O_2.

$$H_2O_2 \xleftrightarrow{UV} 2OH^\bullet$$
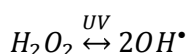
While combined approaches provide better results in most cases, NTP technology appears to surpass its counterparts in terms of pesticide dissipation effects. This is evident from the work of Kim, et al. (2007), who observed that plasma-induced decomposition process is much faster and more efficient than the UV/ozone process, as observed in **Figure 8**. Again this does not come as a surprise, considering the numerous reactive oxygen species (ROS) and reactive nitrogen species (RNS) generated in plasmas.
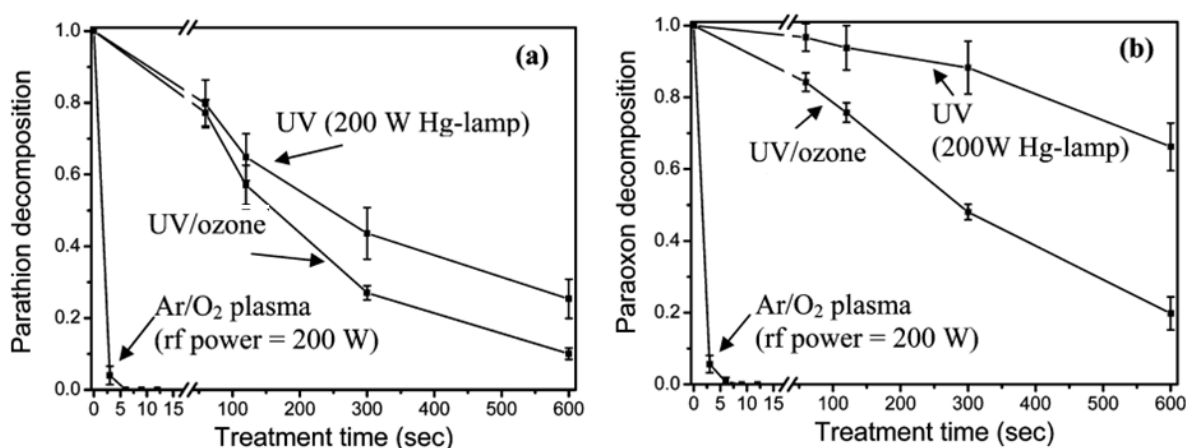

Figure 8 Decomposition rate comparisons for the plasma, UV/ozone, and UV processes for (a) parathion and (b) paraoxon by monitoring the decrease of the nitrobenzyl peak intensities. Adapted from Kim, et al. (2007) by courtesy of ACS publications.

Preprint submitted to Trends in Food Science & Technology

It is crucial to note that combined approaches could only help to increase the rate of the chemical reaction with pesticide and not the diffusion rate coefficient. The latter is decided by the geometry of the reactor and the hydrodynamics or fluid dynamics of the treatment system. Mathematical modelling of the reactors/processors using convection-diffusion-reaction equations will certainly prove useful to draw meaningful conclusions. Significant data has already accumulated in literature in regard to rate coefficients which could prove useful for modelling; c.f. Wojnárovits and Takács (2014) for rate coefficients of hydroxyl radical reactions with pesticide molecules. Despite several reports over last three decades regarding the efficiency of combined AOPs in aqueous systems, the use of such technologies has not been explored for removal of pesticide residues on fruits and vegetables or other foods for that matter of fact. In a recent study, Lin, et al. (2012) observed fast dissipation of cypermethrin, malathion, and dichlorovos from tea leaves subjected to photocatalytic ozonation (i.e. $O_3/UV/TiO_2$) process. A new finding was that the degradation rates on tea leaves were unaffected by pH of the reaction medium, while rates for pesticide degradation in water were affected by the pH. Such unforeseen phenomena should at least be expected when using combined approaches for more complex food systems. The increased cost of the treatment appears to be a possible issue of concern for not exploring such applications for horticultural produce and their products. Significant developments to leverage the synergistic effects of various technologies for chemical decontamination of foods are expected in near future. A decrease in total process time by combining technologies is highly desirable as it would enable retaining the product quality.

10. Future directions

The following considerations are pertinent to the future developments in pesticide breakdown using non-thermal technologies and AOPs.

(1) The mode of action of most advanced oxidation processes overlap. For example, in almost all the cases it has been either confirmed or hypothesised that hydrogen peroxide and hydroxyl radicals form in the aqueous phase, which react with the pesticide residues. Any advancement in the fundamental understanding of one technology is therefore likely to assist in understanding the action of others. For example, the development of a plasma state contributing to sonoluminiscence during ultrasound application and cavitation is reported (Flannigan & Suslick, 2005). Therefore, to begin with and progress towards a deeper understanding of the underlying phenomena the actions of plasma at sub-micron scales can be extended to high power ultrasound applications as a new dimension to the existing theories.

(2) The identification of reaction intermediates and the toxicity determination of the end products of degradation is often quite difficult, considering the number of breakdown products that could form after the treatments (Karaca, et al., 2012). Unavailability of commercial standards of the degraded products also adds to the analytical problems. Pesticide breakdown studies in

Preprint submitted to Trends in Food Science & Technology

model aqueous media and identification by use of state of the art analytical methods (e.g. NMR spectroscopy) should be implemented. Alternative options also include real-time monitoring of the reaction (where feasible) using process analytical technologies (PAT). For example, detailed mechanistic insight into the breakdown of cypermethrin in presence of ozone and hydroxyl radicals has been obtained using real-time Fourier transform infrared spectroscopy (FTIR) (Segal-Rosenheimer, Linker, & Dubowski, 2011). The availability of such data will enable to evaluate the toxicity and stability of the breakdown products relative to the parent molecule. To further substantiate the importance of structural changes versus toxicity, it is worth pointing that chlorine group is considered essential for the toxicity of organochlorine pesticides (OCP) and their by- products. Therefore, the toxicity of OCP is closely related to the extent of de-chlorination achieved (Shah, et al., 2014).

(3) The challenge at present is to increase food production without further pressure on the profitability of farming enterprises and avoiding substantial increases in food prices. This in turn emphasises the need to assess the cost of technologies to dissipate pesticide residues. The electrical energy per unit order (EE/O), defined as the electrical energy which is required for the breakdown of a contaminant of low initial concentration by one order of magnitude in 1 m³ contaminated water is a tool to compare the operating costs of AOPs (Zoschke, Bornick, & Worch, 2014). A paucity of EE/O data does not allow assessing the potential of reported technologies in an industrial set-up. Therefore, such calculations are encouraged.

11. Conclusions

In this review, we presented an overview of the fate of pesticides under the influence of various non-thermal technologies as evidenced by recent literature. In general, information about fate of pesticides during non-thermal processing of foods is limited. Despite being in its infancy, the research progress in this subject has already shown that high pressure processing and pulsed electric field are effective in degrading pesticide residues in fruits, vegetables and/or their products. For liquid foods such as fruit juices, ozone and PEF are promising when compared to ultrasound considering the long processing times required with the latter for effective pesticide degradation. For whole solid foods, such as fresh fruits and vegetables HPP, ozone and cold plasma are promising options. A considerable number of studies have reported the efficacy of AOPs for breakdown of pesticides in food and water; however, information regarding the toxicity of breakdown products is limited. We have indicated in several places within the review that often AOPs share similar mode of action on pesticide molecules, involving radicals and ions which form in aqueous media. Identification of the similarities among reaction mechanisms and pathways offers possibilities of developing approaches that combine effects from different technologies.

Among the AOPs reviewed, non-thermal plasma appears to be very competitive considering the rapid dissipation rates and numerous active chemical species. Combinations of AOPs are also very effective when compared to individual methods. We have remarked that studies to examine the complex mechanisms involved in pesticide breakdown using advanced oxidation and non-thermal technologies need focus to impart practical usability. Finally we emphasised that future investigations be reported under standardised process parameters to facilitate comparisons between studies in terms of both, the effects of process variables on the behaviour of pesticide breakdown, and energy efficiency. Within a modern agricultural production and food processing framework, it is apt to say that non-thermal and AOPs have potential to contribute to the realisation of sustainability.

References

Abramovic, B. F., Banic, N. D., & Sojic, D. V. (2010). Degradation of thiacloprid in aqueous solution by UV and UV/H2O2 treatments. *Chemosphere, 81*, 114-119.

Agarwal, A., Ng, W. J., & Liu, Y. (2011). Principle and applications of microbubble and nanobubble technology for water treatment. *Chemosphere, 84*, 1175-1180.

Al Rashidi, M. J., Chakir, A., & Roth, E. (2013). Heterogeneous ozonolysis of folpet and dimethomorph: a kinetic and mechanistic study. *J Phys Chem A, 117*, 2908-2915.

Autin, O., Hart, J., Jarvis, P., MacAdam, J., Parsons, S. A., & Jefferson, B. (2013). The impact of background organic matter and alkalinity on the degradation of the pesticide metaldehyde by two advanced oxidation processes: UV/H(2)O(2) and UV/TiO(2). *Water Res, 47*, 2041-2049.

Bai, Y., Chen, J., Mu, H., Zhang, C., & Li, B. (2009). Reduction of dichlorvos and omethoate residues by O_2 plasma treatment. *J Agric Food Chem, 57*, 6238-6245.

Bai, Y., Chen, J., Yang, Y., Guo, L., & Zhang, C. (2010). Degradation of organophosphorus pesticide induced by oxygen plasma: effects of operating parameters and reaction mechanisms. *Chemosphere, 81*, 408-414.

Bajwa, U., & Sandhu, K. S. (2014). Effect of handling and processing on pesticide residues in food- a review. *J Food Sci Technol, 51*, 201-220.

Basfar, A. A., Mohamed, K. A., Al-Abduly, A. J., Al-Kuraiji, T. S., & Al-Shahrani, A. A. (2007). Degradation of diazinon contaminated waters by ionizing radiation. *Radiation Physics and Chemistry, 76*, 1474-1479.

Basfar, A. A., Mohamed, K. A., & Al-Saqer, O. A. (2012). De-contamination of pesticide residues in food by ionizing radiation. *Radiation Physics and Chemistry, 81*, 473-478.

Bobkova, E., & Rybkin, V. (2015). Peculiarities of Energy Efficiency Comparison of Plasma Chemical Reactors for Water Purification from Organic Substances. *Plasma Chemistry and Plasma Processing, 35*, 133-142.

Bonnechere, A., Hanot, V., Bragard, C., Bedoret, T., & van Loco, J. (2012). Effect of household and industrial processing on the levels of pesticide residues and degradation products in melons. *Food Addit Contam Part A Chem Anal Control Expo Risk Assess, 29*, 1058-1066.

Brun, O. L., Merlet, N., Croue, J. P., & Doré, M. (1993). Phototransformations de composés phytosanitaires en milieu aqueux. *Sci. Technol. l'Eau, 26*, 97-101.

Burrows, H. D., Canle L, M., Santaballa, J. A., & Steenken, S. (2002). Reaction pathways and mechanisms of photodegradation of pesticides. *Journal of Photochemistry and Photobiology B: Biology, 67*, 71-108.

Chen, F., Zeng, L., Zhang, Y., Liao, X., Ge, Y., Hu, X., & Jiang, L. (2009). Degradation behaviour of methamidophos and chlorpyrifos in apple juice treated with pulsed electric fields. *Food Chemistry, 112*, 956-961.

Chen, J. Y., Lin, Y. J., & Kuo, W. C. (2013). Pesticide residue removal from vegetables by ozonation. *Journal of Food Engineering, 114*, 404-411.

Chowdhury, M. A., Jahan, I., Karim, N., Alam, M. K., Abdur Rahman, M., Moniruzzaman, M., Gan, S. H., & Fakhruddin, A. N. (2014). Determination of carbamate and organophosphorus pesticides in vegetable samples and the efficiency of gamma-radiation in their removal. *Biomed Res Int, 2014*, 145159.

Cin, D. A., & Kroger, M. (1982). Effects of Various Kitchen Heat Treatments, Ultraviolet Light, and Gamma Irradiation on. Mirex Insecticide Residues in Fish. *J Food Sci, 47*, 350-354.

Coles, D., & Frewer, L. J. (2013). Nanotechnology applied to European food production – A review of ethical and regulatory issues. *Trends in Food Science & Technology, 34*, 32-43.

Criegee, R. (1975). Mechanism of Ozonolysis. *Angewandte Chemie International Edition in English, 14*, 745-752.

Deora, N. S., Misra, N. N., Deswal, A., Mishra, H. N., Cullen, P. J., & Tiwari, B. K. (2013). Ultrasound for Improved Crystallisation in Food Processing. *Food Engineering Reviews, 5*, 36-44.

Drzewicz, P., Nalecz-Jawecki, G., Gryz, M., Sawicki, J., Bojanowska-Czajka, A., Gluszewski, W., Kulisa, K., Wolkowicz, S., & Trojanowicz, M. (2004). Monitoring of toxicity during degradation of selected pesticides using ionizing radiation. *Chemosphere, 57*, 135-145.

Ebrahimi, A., Mohammadi, A., Sharifi, Z., Asgari, G., & Attar, H. (2013). Application of several advanced oxidation processes for degradation of 4-chlorophenol from aqueous solution. *International Journal of Environmental Health Engineering, 2*, 38.

EC. (2010). Thematic Strategy on Sustainable Use of Pesticides. In (Vol. 2013): Europa website.

EFSA. (2007). Conclusion regarding the peer review of the pesticide risk assessment of the active substance. In (Vol. 110, pp. 31): European Food Safety Authority.

Evert-Arriagada, K., Hernández-Herrero, M. M., Guamis, B., & Trujillo, A. J. (2014). Commercial application of high-pressure processing for increasing starter-free fresh cheese shelf-life. *LWT - Food Science and Technology, 55*, 498-505.

Falguera, V., Pagán, J., Garza, S., Garvín, A., & Ibarz, A. (2011). Ultraviolet processing of liquid food: A review. Part 1: Fundamental engineering aspects. *Food Research International, 44*, 1571-1579.

Flannigan, D. J., & Suslick, K. S. (2005). Plasma formation and temperature measurement during single-bubble cavitation. *Nature, 434*, 52-55.

Gabler, F. M., Smilanick, J. L., Mansour, M. F., & Karaca, H. (2010). Influence of fumigation with high concentrations of ozone gas on postharvest gray mold and fungicide residues on table grapes. *Postharvest Biology and Technology, 55*, 85-90.

Gaens, W. V., & Bogaerts, A. (2013). Kinetic modelling for an atmospheric pressure argon plasma jet in humid air. *Journal of Physics D: Applied Physics, 46*, 275201.

Ghafoor, M., Misra, N. N., Mahadevan, K., & Tiwari, B. K. (2014). Ultrasound assisted hydration of navy beans (Phaseolus vulgaris). *Ultrasonics Sonochemistry, 21*, 409-414.

Greene, S. A., & Pohanish, R. P. (2005). *Sittig's Handbook of Pesticides and Agricultural Chemicals*. Oxford: William Andrew Publishing.

Heo, N. S., Lee, M. K., Kim, G. W., Lee, S. J., Park, J. Y., & Park, T. J. (2013). Microbial inactivation and pesticide removal by remote exposure of atmospheric air plasma in confined environments. *J Biosci Bioeng*.

Herzallah, S. (2009). Effect of UV-light and γ-irradiation of apple juice on organochlorinated pesticide residues. *Bulletin of Faculty of Agriculture, Cairo University, 60*, 206-212.

Hijosa-Valsero, M., Molina, R., Schikora, H., Muller, M., & Bayona, J. M. (2013). Removal of priority pollutants from water by means of dielectric barrier discharge atmospheric plasma. *J Hazard Mater, 262*, 664-673.

Hua, I., & Pfalzer-Thompson, U. (2001). Ultrasonic Irradiation of Carbofuran. *Water Res, 35*, 1445-1452.

Huang, H.-W., Hsu, C.-P., Yang, B. B., & Wang, C.-Y. (2014). Potential Utility of High-Pressure Processing to Address the Risk of Food Allergen Concerns. *Comprehensive Reviews in Food Science and Food Safety, 13*, 78-90.

Hwang, E.-S., Cash, J. N., & Zabik, M. J. (2001). Postharvest Treatments for the Reduction of Mancozeb in Fresh Apples. *J Agric Food Chem, 49*, 3127-3132.

Iizuka, T., Maeda, S., & Shimizu, A. (2013). Removal of pesticide residue in cherry tomato by hydrostatic pressure. *Journal of Food Engineering, 116*, 796-800.

Iizuka, T., & Shimizu, A. (2013). Removal of pesticide residue from cherry tomatoes by hydrostatic pressure (Part 2). *Innovative Food Science & Emerging Technologies.*

Iizuka, T., Yahata, M., & Shimizu, A. (2013). Potential mechanism involved in removal of hydrophobic pesticides from vegetables by hydrostatic pressure. *Journal of Food Engineering, 119*, 1-6.

Ikeura, H., Hamasaki, S., & Tamaki, M. (2013). Effects of ozone microbubble treatment on removal of residual pesticides and quality of persimmon leaves. *Food Chem, 138*, 366-371.

Ikeura, H., Kobayashi, F., & Tamaki, M. (2011a). Removal of residual pesticide, fenitrothion, in vegetables by using ozone microbubbles generated by different methods. *Journal of Food Engineering, 103*, 345-349.

Ikeura, H., Kobayashi, F., & Tamaki, M. (2011b). Removal of residual pesticides in vegetables using ozone microbubbles. *J Hazard Mater, 186*, 956-959.

Ikeura, H., Kobayashi, F., & Tamaki, M. (2013). Ozone microbubble treatment at various water temperatures for the removal of residual pesticides with negligible effects on the physical properties of lettuce and cherry tomatoes. *J Food Sci, 78*, T350-355.

Jijun, G., Zhonghai, L., Haiyan, Z., Jing, T., & Yinghong, L. (2011). Ozone/Ultrasound Degradation Effect on Residual Pesticides in Commercially Available Apples. In *Bioinformatics and Biomedical Engineering, (iCBBE) 2011 5th International Conference on* (pp. 1-4).

Karaca, H., & Velioglu, Y. S. (2007). Ozone applications in fruit and vegetable processing. *Food Reviews International, 23*, 91-106.

Karaca, H., Walse, S. S., & Smilanick, J. L. (2012). Effect of continuous 0.3μL/L gaseous ozone exposure on fungicide residues on table grape berries. *Postharvest Biology and Technology, 64*, 154-159.

Kaushik, G., Satya, S., & Naik, S. N. (2009). Food processing a tool to pesticide residue dissipation – A review. *Food Research International, 42*, 26-40.

Keikotlhaile, B. M., Spanoghe, P., & Steurbaut, W. (2010). Effects of food processing on pesticide residues in fruits and vegetables: a meta-analysis approach. *Food Chem Toxicol, 48*, 1-6.

Kelly, S., & Turner, M. M. (2014). Generation of reactive species by an atmospheric pressure plasma jet. *Plasma Sources Science and Technology, 23*, 065013.

Khadre, M. A., Yousef, A. E., & Kim, J. G. (2001). Microbiological aspects of ozone applications in food: A review. *Journal of food science, 66*, 1242-1252.

Kim, S. H., Kim, J. H., & Kang, B. K. (2007). Decomposition reaction of organophosphorus nerve agents on solid surfaces with atmospheric radio frequency plasma generated gaseous species. *Langmuir, 23*, 8074-8078.

Kossyi, I. A., Kostinsky, A. Y., Matveyev, A. A., & Silakov, V. P. (1992). Kinetic scheme of the non-equilibrium discharge in nitrogen-oxygen mixtures. *Plasma Sources Science and Technology, 1*, 207.

Koutchma, T., Forney, L. J., & Moraru, C. I. (2010). *Ultraviolet light in food technology: principles and applications*: CRC Press.

Kusvuran, E., Yildirim, D., Mavruk, F., & Ceyhan, M. (2012). Removal of chloropyrifos ethyl, tetradifon and chlorothalonil pesticide residues from citrus by using ozone. *J Hazard Mater, 241-242*, 287-300.

Lafi, W. K., & Al-Qodah, Z. (2006). Combined advanced oxidation and biological treatment processes for the removal of pesticides from aqueous solutions. *J Hazard Mater, 137*, 489-497.

Li, C. F., & Bradley, R. L., Jr. (1968). Degradation of Chlorinated Hydrocarbon Pesticides in Milk and Butteroil by Ultraviolet Energy1. *Journal of Dairy Science, 52*, 27-30.

Lin, L., Xie, M., Liang, Y., He, Y., Sing Chan, G. Y., & Luan, T. (2012). Degradation of cypermethrin, malathion and dichlorovos in water and on tea leaves with O3/UV/TiO2 treatment. *Food control, 28*, 374-379.

Misra, N. N., Kadam, S. U., & Pankaj, S. K. (2011). An overview of nonthermal technologies in food processing. *Indian Food Industry, 30*, 45-52.

Preprint submitted to Trends in Food Science & Technology

Misra, N. N., Keener, K. M., Bourke, P., Mosnier, J. P., & Cullen, P. J. (2014). In-package atmospheric pressure cold plasma treatment of cherry tomatoes. *Journal of Bioscience and Bioengineering, 118*, 177-182.

Misra, N. N., Moiseev, T., Patil, S., Pankaj, S. K., Bourke, P., Mosnier, J. P., Keener, K. M., & Cullen, P. J. (2014). Cold Plasma in Modified Atmospheres for Post-harvest Treatment of Strawberries. *Food and Bioprocess Technology, 7*, 3045-3054.

Misra, N. N., Pankaj, S. K., Bourke, P., & Cullen, P. J. (2013). In-package nonthermal plasma treatment degrades contemporary pesticides on strawberries. In *International Conference on Plasma Science and Applications (ICPSA2013)* (pp. 91-92). Singapore: Nanyang Technological University.

Misra, N. N., Pankaj, S. K., Walsh, T., O'Regan, F., Bourke, P., & Cullen, P. J. (2014). In-package nonthermal plasma degradation of pesticides on fresh produce. *Journal of Hazardous Materials, 271*, 33-40.

Misra, N. N., Patil, S., Moiseev, T., Bourke, P., Mosnier, J. P., Keener, K. M., & Cullen, P. J. (2014). In-package atmospheric pressure cold plasma treatment of strawberries. *Journal of Food Engineering, 125*, 131-138.

Misra, N. N., Tiwari, B. K., Raghavarao, K. S. M. S., & Cullen, P. J. (2011). Nonthermal Plasma Inactivation of Food-Borne Pathogens. *Food Engineering Reviews, 3*, 159-170.

Misra, N. N., Ziuzina, D., Cullen, P. J., & Keener, K. M. (2013). Characterization of a novel atmospheric air cold plasma system for treatment of packaged biomaterials. *Transactions of the ASABE, 56*, 1011-1016.

Mohamed, K. A., Basfar, A. A., Al-Kahtani, H. A., & Al-Hamad, K. S. (2009). Radiolytic degradation of malathion and lindane in aqueous solutions. *Radiation Physics and Chemistry, 78*, 994-1000.

Moiseev, T., Misra, N. N., Patil, S., Cullen, P. J., Bourke, P., Keener, K. M., & Mosnier, J. P. (2014). Post-discharge gas composition of a large-gap DBD in humid air by UV–Vis absorption spectroscopy. *Plasma Sources Science and Technology, 23*, 065033.

Mostafalou, S., & Abdollahi, M. (2013). Pesticides and human chronic diseases: evidences, mechanisms, and perspectives. *Toxicol Appl Pharmacol, 268*, 157-177.

Nieto, L. M., Hodaifa, G., & Casanova, M. S. (2009). Elimination of pesticide residues from virgin olive oil by ultraviolet light: preliminary results. *J Hazard Mater, 168*, 555-559.

Norton, T., & Sun, D. W. (2008). Recent Advances in the Use of High Pressure as an Effective Processing Technique in the Food Industry. *Food and Bioprocess Technology, 1*, 2-34.

O'Donnell, C., Tiwari, B. K., Cullen, P., & Rice, R. G. (2012). *Ozone in food processing*: John Wiley & Sons.

Ong, K. C., Cash, J. N., Zabik, M. J., Siddiq, M., & Jones, A. L. (1996). Chlorine and ozone washes for pesticide removal from apples and processed apple sauce. *Food Chemistry, 55*, 153-160.

Pankaj, S. K., Bueno-Ferrer, C., Misra, N. N., Milosavljević, V., O'Donnell, C. P., Bourke, P., Keener, K. M., & Cullen, P. J. (2014). Applications of cold plasma technology in food packaging. *Trends in Food Science & Technology, 35*, 5-17.

Pankaj, S. K., Bueno-Ferrer, C., Misra, N. N., O'Neill, L., Jiménez, A., Bourke, P., & Cullen, P. J. (2014). Characterization of polylactic acid films for food packaging as affected by dielectric barrier discharge atmospheric plasma. *Innovative Food Science & Emerging Technologies, 21*, 107-113.

Rastogi, N. K. (2011). Opportunities and challenges in application of ultrasound in food processing. *Crit Rev Food Sci Nutr, 51*, 705-722.

Rastogi, N. K., Raghavarao, K. S. M. S., Balasubramaniam, V. M., Niranjan, K., & Knorr, D. (2007). Opportunities and Challenges in High Pressure Processing of Foods. *Critical Reviews in Food Science and Nutrition, 47*, 69-112.

Reynolds, G., Graham, N., Perry, R., & Rice, R. G. (1989). Aqueous Ozonation of Pesticides: A Review. *Ozone: Science & Engineering, 11*, 339-382.

Schramm, J. D., & Hua, I. (2001). Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism. *Water Res, 35*, 665-674.

Preprint submitted to Trends in Food Science & Technology

Segal-Rosenheimer, M., Linker, R., & Dubowski, Y. (2011). Heterogeneous oxidation of the insecticide cypermethrin as thin film and airborne particles by hydroxyl radicals and ozone. *Phys Chem Chem Phys, 13*, 506-517.

Segat, A., Misra, N. N., Fabbro, A., Buchini, F., Lippe, G., Cullen, P. J., & Innocente, N. (2014). Effects of ozone processing on chemical, structural and functional properties of whey protein isolate. *Food Research International, 66*, 365-372.

Shah, N. S., He, X., Khan, H. M., Khan, J. A., O'Shea, K. E., Boccelli, D. L., & Dionysiou, D. D. (2013). Efficient removal of endosulfan from aqueous solution by UV-C/peroxides: A comparative study. *J Hazard Mater, 263, Part 2*, 584-592.

Shah, N. S., Khan, J. A., Nawaz, S., & Khan, H. M. (2014). Role of aqueous electron and hydroxyl radical in the removal of endosulfan from aqueous solution using gamma irradiation. *J Hazard Mater, 278C*, 40-48.

Shen, J., Sun, Q., Zhang, Z., Cheng, C., Lan, Y., Zhang, H., Xu, Z., Zhao, Y., Xia, W., & Chu, P. K. (2014). Characteristics of DC Gas-Liquid Phase Atmospheric-Pressure Plasma and Bacteria Inactivation Mechanism. *Plasma Processes and Polymers*.

Shriwas, A. K., & Gogate, P. R. (2011). Ultrasonic degradation of methyl Parathion in aqueous solutions: Intensification using additives and scale up aspects. *Separation and Purification Technology, 79*, 1-7.

Tizaoui, C., Mezughi, K., & Bickley, R. (2011). Heterogeneous photocatalytic removal of the herbicide clopyralid and its comparison with UV/H2O2 and ozone oxidation techniques. *Desalination, 273*, 197-204.

Walse, S. S., & Karaca, H. (2011). Remediation of Fungicide Residues on Fresh Produce by Use of Gaseous Ozone. *Environmental Science & Technology, 45*, 6961-6969.

Wang, Y., Yang, B., Zhang, P., Zhang, W., Liu, C., Shu, X., & Shu, J. (2012). Heterogeneous reactions of pirimiphos-methyl and pirimicarb with NO3 radicals. *J Phys Chem A, 116*, 10802-10809.

Wen, H. W., Hsieh, M. F., Wang, Y. T., Chung, H. P., Hsieh, P. C., Lin, I. H., & Chou, F. I. (2010). Application of gamma irradiation in ginseng for both photodegradation of pesticide pentachloronitrobenzene and microbial decontamination. *J Hazard Mater, 176*, 280-287.

Wesseling, C., Corriols, M., & Bravo, V. (2005). Acute pesticide poisoning and pesticide registration in Central America. *Toxicol Appl Pharmacol, 207*, 697-705.

Whangchai, K., Uthaibutra, J., Phiyanalinmat, S., Pengphol, S., & Nomura, N. (2011). Effect of Ozone Treatment on the Reduction of Chlorpyrifos Residues in Fresh Lychee Fruits. *Ozone: Science & Engineering, 33*, 232-235.

Wojnárovits, L., & Takács, E. (2014). Rate coefficients of hydroxyl radical reactions with pesticide molecules and related compounds: A review. *Radiation Physics and Chemistry, 96*, 120-134.

Wu, C., & Linden, K. G. (2010). Phototransformation of selected organophosphorus pesticides: roles of hydroxyl and carbonate radicals. *Water Res, 44*, 3585-3594.

Wu, J., Luan, T., Lan, C., Hung Lo, T. W., & Chan, G. Y. S. (2007). Removal of residual pesticides on vegetable using ozonated water. *Food control, 18*, 466-472.

Wu, J. G., Luan, T. G., Lan, C. Y., Lo, W. H., & Chan, G. Y. S. (2007). Efficacy evaluation of low-concentration of ozonated water in removal of residual diazinon, parathion, methyl-parathion and cypermethrin on vegetable. *Journal of Food Engineering, 79*, 803-809.

Yao, J. J., Gao, N. Y., Li, C., Li, L., & Xu, B. (2010). Mechanism and kinetics of parathion degradation under ultrasonic irradiation. *J Hazard Mater, 175*, 138-145.

Zhang, H. Q., Barbosa-Cánovas, G. V., Balasubramaniam, V. M., Patrick Dunne, C., Farkas, D. F., & Yuan, J. T. C. (2010). *Nonthermal Processing Technologies for Food*. Oxford, UK: Wiley-Blackwell.

Zhang, J., Zheng, Z., Zhao, T., Zhao, Y., Wang, L., Zhong, Y., & Xu, Y. (2008). Radiation-induced reduction of diuron by gamma-ray irradiation. *J Hazard Mater, 151*, 465-472.

Zhang, Y., Hou, Y., Chen, F., Xiao, Z., Zhang, J., & Hu, X. (2011). The degradation of chlorpyrifos and diazinon in aqueous solution by ultrasonic irradiation: effect of parameters and degradation pathway. *Chemosphere, 82*, 1109-1115.

Preprint submitted to Trends in Food Science & Technology

Zhang, Y., Hou, Y., Zhang, Y., Chen, J., Chen, F., Liao, X., & Hu, X. (2012). Reduction of diazinon and dimethoate in apple juice by pulsed electric field treatment. *J Sci Food Agric, 92*, 743-750.

Zhang, Y., Xiao, Z., Chen, F., Ge, Y., Wu, J., & Hu, X. (2010). Degradation behavior and products of malathion and chlorpyrifos spiked in apple juice by ultrasonic treatment. *Ultrason Sonochem, 17*, 72-77.

Zhang, Y., Zhang, W., Liao, X., Zhang, J., Hou, Y., Xiao, Z., Chen, F., & Hu, X. (2010). Degradation of diazinon in apple juice by ultrasonic treatment. *Ultrason Sonochem, 17*, 662-668.

Zhang, Y., Zhang, Z., Chen, F., Zhang, H., & Hu, X. (2012). Effect of sonication on eliminating of phorate in apple juice. *Ultrason Sonochem, 19*, 43-48.

Zhu, W.-C., Wang, B.-R., Xi, H.-L., & Pu, Y.-K. (2010). Decontamination of VX Surrogate Malathion by Atmospheric Pressure Radio-frequency Plasma Jet. *Plasma Chemistry and Plasma Processing, 30*, 381-389.

Zoschke, K., Bornick, H., & Worch, E. (2014). Vacuum-UV radiation at 185 nm in water treatment--a review. *Water Res, 52*, 131-145.

Preprint submitted to Trends in Food Science & Technology