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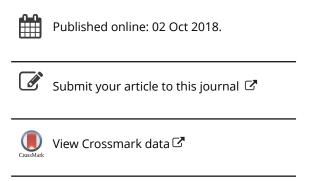
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# Recent advancements in the application of nonthermal plasma technology for the seafood industry

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#### **REVIEW**



# Recent advancements in the application of non-thermal plasma technology for the seafood industry

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#### **ABSTRACT**

Non-thermal plasma (NTP) is one of the most promising minimal processing methods for the food industry. However up until recently there are limited studies which would report the application and effect of NTP on processed seafood. The objective of this review is to highlight the recent findings and advancements in the application of NTP within the fish and other seafood industry, including direct application of fresh and dried fish and seafood with as well as indirect application of plasma activated water and seafood industry wastewater purification. The article also summarizes the effect of plasma treatment on microbiological quality, physicochemical and sensory properties and oxidation rate of treated fish and seafood. NTP has high potential to be used within various fields of seafood industry. It is especially effective in treatment of dried seafood products, but the use of plasma activated water during various processing steps such as seafood washing could be also beneficial. Moreover NTP could also be used as a cost effective and environmentally friendly method for seafood wastewater purification.

#### **KEYWORDS**

cold plasma; non-thermal plasma; fish; seafood; shelflife; oxidation

#### Introduction

Non-thermal plasma (NTP) is modern cost effective and environmental friendly method which is gaining popularity within various types of industry. It has been successfully applied in medicine, agriculture, environment protection or energy and textile industries (Table 1). The technology has also gained much interest in possible application within the food industry (Mir et al. 2016; Pankaj et al. 2014; Thirumdas et al. 2015; Misra et al. 2016). Fresh fish and other seafood however were often regarded as not suitable for this treatment due to possibility of increased oxidation rate, which might lead to accelerated spoilage and development of off-flavors and off-odors (Misra et al. 2011). In the last few years, research has demonstrated the effect of NTP on fresh, dried fish and seafood, focusing not only on antibacterial properties but also on the increase in oxidation rate, fatty acids composition, sensory attributes or physicochemical properties of the treated product. The aim of this manuscript is to summarize those recent findings and evaluate the efficiency and potential of using NTP on fish and seafood products.

## What is non-thermal plasma and how it works

The non-thermal plasma, also called cold plasma, is a partially ionized gas, like any other plasma, but with energy (temperature) stored mostly in electrons and not in gas (Scholtz et al.

2015; Moreau et al. 2008). The formation of plasma can be generally achieved by two methods. The first method is by heating the gas to high temperatures of approximately 1,000 – 10,000 K, during which thermal plasma, with electron temperature of around 10,000 K, is formed (Samal 2017). Due to high temperatures this type of plasma is not suitable for use on a range of food products. The second method of plasma generation is through applying high-energy electric field which disrupts and breaks-down the equilibrium state of the gas by formation of ions and electrons (Misra et al. 2015). This method results in formation of non-thermal plasma. As name suggests the temperature of this type of plasma is close to ambient temperature, and does not heat the surface of the treated product (Fridman et al. 2007).

There are two types of NTP formation equipment, depending on the pressure conditions: lower pressure plasma systems and atmospheric conditions plasma systems. Due to the low-pressure requirement (vacuum) for plasma to be created, the low-pressure plasma systems have not been widely used for food treatment. In recent years however there has been a substantial development of atmospheric pressure plasma systems, which enables to treat food samples in a more easier and cost-effective manner (Misra et al. 2011). The commonly used cold plasma systems include dielectric barrier discharge (DBD) and atmospheric pressure plasma jet (APPJ).

In food industry the NTP is mainly used as a minimal processing preservation method, which reduces the risk of

Table 1. Examples of cold plasma applications not related to food processing.

Field	Application	References
Environment protection	Purification of water systems from pharmaceutical residues	Magureanu et al. (2015)
	Purification of engines exhaust gases from $NO_x$	Talebizadeh et al. (2014)
	Enhancing the efficiency of filters (for example activated carbon or biochar filters) to filter flue gases	Zhang et al. (2015)
		Wang et al. (2018)
	Purification of textile industry wastewater from dyes	Ghodbane et al. (2014)
Medicine	Wound healing enhancement	Haertel et al. (2014)
	Cancer treatment	Toyokuni et al. (2016)
	Endometriosis treatment	Ishida et al. (2016)
Energy	Syngas production from carbon dioxide reforming	Yap et al. (2018)
		Estifaee et al. (2014)
Agriculture	Enhancement of germination and seedling growth of seeds	Randeniya and de Groot (2015)
Nanotechnology	Metal nanoparticles formation	Borra et al. (2015)

microbiological contamination and spoilage. There is a number of mechanisms through which the food decontamination during NTP treatment is achieved, namely: (i) formation of reactive species (RS); (ii) UV radiation; (iii) formation of charged particles and (iv) formation of ozone (in case of treatments with oxygen atmosphere) (Guo et al. 2015). The effect of each of those mechanisms on the decontamination and the efficiency of the overall decontamination process depends on: (i) type of plasma generation unit; (ii) type of product decontaminated; (iii) parameters of the plasma generation (mainly voltage, frequency and time) (iv) the gas atmosphere in which the product is being held; (v) exposure mode (direct or indirect) and (vi) microorganism species (Liao et al. 2017). The general rules for improving efficiency are: (i) higher voltage and frequency of the generated electric field increases the treatment efficiency since this results in higher energy density of plasma; (ii) longer exposure time results in better decontamination efficiency; (iii) direct exposure of food product on the plasma is more efficient the indirect exposure (outside of plasma discharge zone) and (iv) gram-negative bacteria are more susceptible to NTP treatment than gram-positive bacteria (Liao et al. 2017). It is important to mention however that from each of those rules there are exceptions. Kulawik et al. (2018) treated salmon sushi samples stored in air with NTP using 70 and 80 kV voltage for 5 min. They observed no significant differences in total viable counts between those two groups through whole 11 days of storage, which suggests that there is a threshold of voltage after which the efficiency is not increased. Also there seems to be a time threshold after which increasing the treatment time will not results in increased reduction. Rød et al. (2012) treated dry-cured beef inoculated with Listeria innocua using NTP in 30/70% oxygen/argon atmosphere and observed that prolonging plasma exposure time from 20 to 60 s did not further reduce the L. innocua loads. Even more interesting, the authors observed that shorter (20 s) treatments, which were repeated for 3 times with 10 min intervals, yielded much more significant inhibition. Although most authors are in agreement that direct exposure of samples to plasma is more effective, Lu et al. (2014) observed that indirect exposure to NTP resulted in higher decrease in E. coli and L. monocytogenes than direct exposure. The authors hypothesized that it might be due to recombination of formed radicals, which resulted in formation of more effective RS such as ozone. Moreover the authors observed that gram-positive bacteria (L.

monocytogenes) were more susceptible than gram-negative bacteria (E. coli) which is surprising, since due to lower thickness of peptidoglycan layer, gram-negative bacteria are usually more affected by NTP (Liao et al. 2017).

One of the most important factors that influence the efficiency of NTP treatment is the gas mixture used and relative humidity. Depending on the mixture and humidity, different decontamination factors are formed, which in turn affects the effectiveness of the treatment. The main decontamination agents seem to be oxygen reactive species (ROS) from which ozone, hydrogen peroxide, singlet oxygen and OH radicals seem to be most important (Guo et al. 2015). Although NTP generated in other gas mixtures than oxygen also leads to formation of RS, for example NTP in nitrogen results in formation of reactive nitrogen species such as NO, NO<sub>2</sub> and NO<sub>3</sub> (Chauvin et al. 2017), in general the addition of oxygen into the atmosphere increases the efficiency of the decontamination (Eto et al. 2008; Patil et al. 2014). It should be however noted that some studies suggest that exceeding certain threshold of oxygen in the gas mixture may decrease the effectiveness of the decontamination. Uhm et al. (2007) demonstrated that the disinfection peak for Bacillus atrophaeus was observed when oxygen content reached 0.15% in Ar/O<sub>2</sub> gas mixture and Deng et al. (2006) reported decreased efficiency of NTP treatment when He/O2 gas mixture was used instead of pure He. Moreover the lack of moisture decreases the efficiency of the treatment, mainly because it leads to reduced formation of OH radicals, with main disinfection agents being UV radiation and ozone (Eto et al. 2008; Patil et al. 2014).

The NTP treatment despite having tremendous advantages has one disadvantage which might limit its industrial application. As described before, NTP causes the formation of various RS, ozone, UV radiation or charged particles which are responsible for reported decontamination effect, but also can induce oxidation of the food products and destroy light sensitive compounds. This might result in degradation of various antioxidant food components such as flavonoids or vitamins (Misra et al. 2011), however many authors report that this degradation effect is minimal. Wang et al. (2012) treated carrot and pear using plasma jet cold plasma system with atmospheric air environment and observed very low decrease in vitamin C ranging from 2.8 to 3.2%. Rodríguez et al. (2017) measured vitamin C content in indirect cold plasma treated cashew apple juice using nitrogen atmosphere and reported the decrease (by 12.2%)

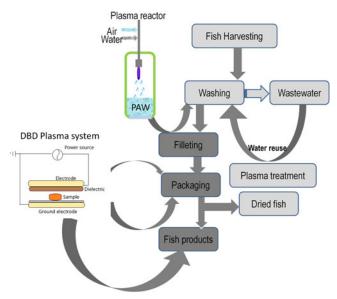


Figure 1. Schematics of the use of plasma in fish and seafood industry.

only after prolonged exposure time of 15 min at the highest gas flow rate of 50 ml/min. Moreover they found that plasma treatment not only did not reduce total phenolic and flavonoid content but in some cases treatments increased their content, which was attributed to the fact that some of those compounds were bound within cell membranes and were freed by the energy provided from the plasma treatment. Also Ramazzina et al. (2015) observed no significant differences in vitamin C and total phenolic content of NTP treated kiwifruits. Although the changes in vitamins and various anitioxidant compounds appears to be low or insignificant, there is a also a matter of fatty acids oxidation which is an important issue of meat and fish products (Misra et al. 2011).

The NTP treatment can be applied at various processing stages within fish and other seafood industry i.e. surface decontamination using plasma activated water and treatment of the final product, through packages and wastewater treatment. The schematic illustrating the possible application of NTP during various processing steps within seafood industry is shown on Figure 1.

# The use of non-thermal plasma for preservation of fresh fish and seafood

The summary of antimicrobial properties of NTP treatment of fish and seafood are shown in Table 2, while the effect of NTP treatment on quality properties and oxidation rate of treated fish and seafood is shown in Table 3.

Although NTP affects the microbial counts of treated fish and seafood, the efficiency of the method is still disputed. It is worth mentioning that the antibacterial efficiency of NTP treatment is usually lower when treatment is applied to food products than on plain surface. This has been observed by Chiper et al. (2011) who noted that NTP treatment of cold smoked salmon slices inoculated with Photobacterium phosphoreum and Lactobacillus sakei was less significant than on agar slabs. Moreover NTP treatment have not been effective

against L. monocytogenes on both cold smoke salmon and on agar slabs, which might limit the possible use of this method in fish and seafood industry, since L. monocytogenes is one of the main pathogens related to fish and seafood products (Farber 1991).

Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017) used DBD plasma system to treat fresh mackerel fillets (50 Hz, 70 and 80 kV, time 1,3 and 5 min, air atmosphere) and observed that while NTP did not affect the loads of total aerobic mesophilic bacteria, it had significant effect on psychrotrophic, lactic acid bacteria (LAB) and Pseudomonas counts with treatment being more effective with increasing time and discreet voltage, with the latter more effective in reduction of LAB and Pseudomonas. In case of the most effective treatments, the reductions in all studied bacteria loads reached up to 2 log cfu/g. Although the NTP treatment did not affect the proximate composition and color, with the exception of slight increase in lightness, it induced the oxidation of mackerel fillets. The treatment resulted in over 5-fold increase in peroxide value and almost 4-fold increase in dienes, with both exposure time and voltage affecting the rate of oxidation. Surprisingly, at the same time the TBARS analysis showed no significant differences. The NTP treatment significantly affected the fatty acids composition, increasing the content of oleic and eicosapentaenoic acids, while decreasing the content of palmitic acid and, in case of 80 kV, 5 min treatment, docosahexaenoic acid. Moreover the plasma treatment affected the protein structure and water distribution within the mackerel fillet, reducing the amount of immobilized water within myofibrillar meat proteins. Similar experiment investigated the effect of NTP (DBD system, 70 and 80 kV, 50 Hz, 5 min) on the microbiological load, oxidation rate and quality parameters of air packed Atlantic herring stored in refrigerated conditions for 11 days (Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, and Rico 2017). The authors reported that treatment with higher voltage was significantly more efficient in reduction of microbiological loads. The 70 kV treatment was also not effective in reduction of aerobic mesophilic counts, while 80 kV treatment significantly reduced the loads of those bacteria. The NTP treatment was effective in reduction of psychrotrophic and lactic acid bacteria counts as well as Pseudomonas and Enterobacteriacea counts. On the other hand the 80 kV treatment resulted in higher oxidation rate, measured by TBARS analysis, which might resulted in formation of off-flavours after 6 days of storage. Moreover the NTP treatment significantly affected the color parameters of the fish, causing significant reduction in lightness and redness while significantly increasing yellowness. Those changes were probably due to oxidation of heme proteins of the herring fillet. As in previous experiment with mackerel also in this study the authors observed reduction of water immobilized by myofibrillar proteins. The reduction of immobilized water in two separate studies on two different fish fillets, suggests that NTP treatment might result in lower water holding capacity of fish fillets and water leak during storage, especially of fillets with

Table 2. The antimicrobial properties of NTP treatment on fish and seafood products.

Product	NTP parameters	Plasma working gas	Types of microorganism	Main findings	References
Dried laver	Corona discharge plasma jet system; 20 kV; 58 kHz	Air	Aerobic bacteria;	2.0 log cfu/g reduction after 20 min treatment D value of 7.03 min	Kim et al. (2015)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz 1, 2 and 3 min	Air	Aerobic bacteria	2 log cfu/g reduction after 3 min treatment. D value of 1.47 min	Choi et al. (2017)
Dried Alaska pollock shreds	Corona discharge plasma jet system; 20 kV; 58 kHz; 1, 2 and 3 min	Air	Aerobic bacteria	>2 log cfu/g reduction after 3 min D value of 1,22 min	Choi et al. (2016)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Aerobic bacteria	>3 log cfu/g reduction after 10 min D value of 3.22 min	Puligundla et al. (2017)
Salmon nigiri and hosomaki	Dielectric barrier discharge system; 70 and 80 kV, 50 kHz; 5 min	Air	Aerobic bacteria	No significant reductions observed during 11 days of storage at 4°C	Kulawik et al. (2018)
Dried laver	Corona discharge plasma jet system; 20 kV; 58 kHz	Air	Yeasts and molds	1.2 log cfu/g reduction after 20 min treatment D value of 12.29 min	Kim et al. (2015)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Yeasts and molds	approx. 1 log cfu/g reduction after 3 min treatment. D value of 2.74 min	Choi et al. (2017)
Dried Alaska pol- lock shreds	Corona discharge plasma jet system; 20 kV; 58 kHz; 1, 2 and 3 min	Air	Yeasts and molds	>1 log cfu/g reduction after 3 min treatment. D value of 2.39 min	Choi et al. (2016)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Yeasts and molds	>3 log cfu/g reduction after 10 min <i>D</i> value of 3.25 min	Puligundla et al. (2017)
Dried laver	Corona discharge plasma jet system; 20 kV; 58 kHz	Air	Marine bacteria	1.5 log cfu/g reduction after 20 min treatment D value of 6.93 min	Kim et al. (2015)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Marine bacteria	>1.5 log cfu/g reduction after 3 min treatment. D value of 1.83 min	Choi et al. (2017)
Dried Alaska pollock shreds	Corona discharge plasma jet system; 20 kV; 58 kHz; 1, 2 and 3 min	Air	Marine bacteria	>1.5 log cfu/g reduction after 3 min treatment. D value of 1.71 min	Choi et al. (2016)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Marine bacteria	>3 log cfu/g reduction after 10 min D value of 2.69 min	Puligundla et al. (2017)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Coliform bacteria	2 log cfu/g reduction after 10 min D value of 6.00 min	Puligundla et al. (2017)
Gimbap produced from treated dried laver	Corona discharge plasma jet system; 20 kV; 58 kHz	Air	Aerobic bacteria; Yeasts and molds; Marine bacteria	3-4 log cfu/g reduction in loads of all studied microorganisms after 72 h storage in 25°C	Kim et al. (2015)
Fresh mackerel fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 kHz; treatment time 1, 3 and 5 min	Air	Total aerobic mesophilic bacteria	No significant reduction between treated and untreated samples	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017)
Fresh Atlantic herring fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 kHz; treatment time 5 min	Air	Total aerobic mesophilic bacteria	Significant reduction caused by 80 kV treatment and while 70 kV was found ineffective	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, and Rico (2017)
Fresh mackerel fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 kHz; treatment time 1, 3 and 5 min	Air	Psychrotrophic bacteria; Lactic acid bacteria; Pseudomonas	Significant (but bellow 2 log cfu/g) reductions in loads of all three bacteria groups. Positive correlation between both time and voltage and inhibition rate.	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017)
Fresh Atlantic herring fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 kHz; treatment time 5 min	Air	Psychrotrophic bacteria; Lactic acid bacteria; Pseudomonas; Enterobacteriacea	Significant reduction caused by NTP treatment. Positive correlation between voltage and reduction rate.	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017)
Cold smoked salmon slices	Dielectric barrier discharge system; 11 and 13 kV; 16 kHz; 1 and 2 min	100% Ar; 93% Ar /7% CO <sub>2</sub>	P. phosphoreum (previously inoculated on the surface)	Up to $\approx 3$ and $\approx 1$ log cfu/g reduction at day 0 and 13 respectively. Longer treatment time influenced efficiency but addition of $CO_2$ to plasma working gas not	Chiper et al. (2011)

Table 2. Continued.

Product	NTP parameters	Plasma working gas	Types of microorganism	Main findings	References
Cold smoked salmon slices	Dielectric barrier discharge system; 11 and 13 kV; 16 kHz; 1 and 2 min	100% Ar; 93% Ar /7% CO <sub>2</sub>	L. monocytogenes; L. sakei (both previously inoculated on the surface)	No significant differences between treated and untreated samples	Chiper et al. (2011)
Dried filefish fillets	Not specified; treatment time 3, 5, 10 and 20 min	Air	C. cladosporioides (previously inoculated on the surface)	1.27 log cfu/g reduction after 20 min treatment; D value of 9.32 min; Longer treatment time influenced efficiency	Park and Ha (2015)
Dried filefish fillets	Not specified; treatment time 3, 5, 10 and 20 min	Air	P. citrinum (previously inoculated on the surface)	1.46 log cfu/g reduction after 20 min treatment; D value of 7.42 min; Longer treatment time influenced efficiency	Park and Ha (2015)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Staphylococcus spp.	<1 log cfu/g reduction after 3 min treatment. D value of 3.12 min	Choi et al. (2017)
Dried Alaska pollock shreds	Corona discharge plasma jet system; 20 kV; 58 kHz; 1, 2 and 3 min	Air	Staphylococcus spp.	1 log cfu/g reduction after 3 min treatment. <i>D</i> value of 2.58 min	Choi et al. (2016)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Staphylococcus spp.	>3 log cfu/g reduction after 10 min <i>D</i> value of 3.16 min	Puligundla et al. (2017)

injected brine, however more studies would be necessary to confirm this.

The NTP treatment was also evaluated as a possible method to improve the shelf-life of salmon sushi (nigiri and hosomaki) by reduction of total aerobic bacteria. Both sushi samples were treated using DBD plasma system using 70 and 80 kV voltage and 50 Hz frequency for 5 min and stored at 4°C for 11 days. The study showed no significant differences in total aerobic counts between treated and untreated groups throughout the whole storage period. The treatment increased the oxidation rate of sushi by significantly increasing the TBARS value, with higher voltage resulting in slightly higher oxidation rate, but no significant differences in fatty acids composition was observed (Kulawik et al. 2018).

There is still limited amount of research performed on the effect of NTP on fresh seafood. However, based on the existing data, NTP treatment is not to be the most effective method to improve the shelf-life of fresh seafood, since the microbiological contamination reduction is often limited, and the treatment increases significantly the oxidation rate of the samples. On the other hand, future research could investigate the effect of NTP used in hurdle with other nonthermal methods since it might improve the overall effectiveness of the process.

# The use of non-thermal plasma for preservation of dried fish and seafood

NTP seems to be an effective method for decontamination of dried fish and seafood. Choi et al. (2017) and Choi et al. (2016) studied the effect of NTP on dried squid (Todarodes pacificus) and Alaska pollock shreds treated with a corona discharge plasma jet system (20 kV; 58 kHz; air atmosphere) for up to 3 min. Both studies show similar findings with linear relationship between the treatment time and reduction

of aerobic bacteria, marine bacteria, yeasts and molds and Staphylococcus spp. The treatment also affected physicochemical properties of the dried squid and Alaska Pollock shreds, significantly reducing the moisture content and water activity with water activity after 3 min reaching 0.51 and 0.36 for squid and Alaska pollock respectively. Since no organisms can grow on the products with water activity bellow 0.6 (Pitt and Hocking 2009) the NTP treatment should effectively inhibit any further microbiological spoilage of dried fish and seafood shreds. On the other hand NTP treatment of dried squid and Alaska pollock significantly increased oxidation rate of the samples and 2 and 3 minute treatments caused distinct changes in color parameters of dries squid shreds, mainly reducing lightness. Those changes were however not noticeable for the human eye since the sensory assessment in both studies did not show any significant changes in appearance, color, flavour, taste or overall acceptance. The treatment also did not affect the pH nor TVB-N (total volatile basic nitrogen) of the dried fish and seafood samples (Choi et al. 2017, 2016).

Kim et al. (2015) studied the effect of corona discharge plasma jet (20 kV, 58 Hz, air atmosphere) on the microbial contamination of dried laver and observed the reduction of aerobic bacteria, yeast and molds and marine bacteria by 2, 1.2 and 1.5 log cfu/g respectively after 20 min treatment. When the same dried laver was used to produce gimbap, a Korean dish which consists of dried laver and white rice, they observed 3-4 log reductions for all studied microorganisms during 72 h storage in 25 °C. They have also observed that inactivation kinetics of all studied microorganisms decreases after 10 min of treatment. At the same time they noticed that even prolonged exposure to NTP did not significantly affect the color parameters, total phenolic content (TPC) nor DPPH radical scavenging activity of the dried laver and no significant difference in sensory scores was observed between treated and untreated gimbap.



Table 3. The effect of NTP on quality properties and oxidation rate of fish and seafood products

Product	NTP parameters	Plasma working gas	Parameter	Main findings	References
Dried laver	Corona discharge plasma jet system; 20 kV; 58 kHz	Air	Color	No differences between treated and	Kim et al. (2015)
Fresh mackerel fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 1, 3 and 5 min	Air	Color	untreated products Significant but slight reduction in lightness. No affect on redness and yellowness	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017)
Fresh Atlantic herring fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 5 min	Air	Color	Significant reduction in lightness and redness while significant increase in yellowness throughout 11 days of storage	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, and Rico (2017)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Color	Significant changes in L* after 3 min; AE shows distinct changes in color parameters after 3 min and longer	Choi et al. (2017)
Dried Alaska pollock shreds	Corona discharge plasma jet system; 20 kV; 58 kHz; 1, 2 and 3 min	Air	Color	No significant changes in individual color parameters between treated and untreated samples. ΔE shows distinct changes in color parameters after 3 min	Choi et al. (2016)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Color	NTP treatment for 7 min and longer significantly improved lightness and redness, and 10 min treatment also significantly increased yellowness. ΔE shows very distinct changes in color parameters after 7 min treatment	Puligundla et al. (2017)
Fresh mackerel fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 1, 3 and 5 min	Air	рН	Slight increase in pH (approx 0.1) in case of 80kV, 5 min treatment. No changes observed for other treatments	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017)
Fresh Atlantic herring fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 5 min	Air	рН	NTP treatment caused significant initial drop in pH (by approx 0.1) and the lower pH was maintained through 8 days of storage (by 0.1 – 0.3)	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, and Rico (2017)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	рН	No significant changes between treated and untreated samples.	Choi et al. (2017)
Dried Alaska pollock shreds	Corona discharge plasma jet system; 20 kV; 58 kHz; 1, 2 and 3 min	Air	рН	Slight but significant reduction in pH (by approx 0.1) after treatment.	Choi et al. (2016)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	pH	No significant changes between treated and untreated samples	Puligundla et al. (2017)
Fresh mackerel fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 1, 3 and 5 min	Air	Proximate composition, protein structure and water distribution	No changes in proximate composition, NTP treatment caused reduction of immobilized water within myofibrillar proteins	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017)
Fresh Atlantic herring fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 5 min	Air	Protein structure and water distribution	NTP treatment caused reduction of immobilized water within myofibrillar proteins	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, and Rico (2017)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Moisture content; Water activity	Significant reduction in moisture content by 10 and 15% after 2 and 3 min. Significant reduction in aw by 19, 25 and 28% after 1, 2 and 3 min	Choi et al. (2017)

Table 3. Continued.

Product	NTP parameters	Plasma working gas	Parameter	Main findings	References
Dried Alaska pollock shreds	Corona discharge plasma jet system; 20 kV; 58 kHz 1, 2 and 3 min	Air	Moisture content; Water activity	Significant reduction in moisture content by 37, 53 and 55% after 1, 2 and 3 min. Significant reduction in aw by 15, 31 and 41% after 1, 2 and 3 min	Choi et al. (2016)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Moisture content; Water activity	No significant changes between treated and untreated samples	Puligundla et al. (2017)
Gimbap produced from treated dried laver	Corona discharge plasma jet system; 20 kV; 58 kHz	Air	Sensory parameters	No significant differences between any of the sensory parameters between treated and untreated samples	Kim et al. (2015)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Sensory parameters	No significant differences in any of the sensory parameters between treated and untreated samples	Choi et al. (2017)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Sensory parameters	Significant increase in texture scores after 3 min treatment. No significant differences in other sensory parameters between treated and untreated samples	Choi et al. (2016)
Dried filefish fillets	Not specified; treatment time 3, 5, 10 and 20 min	Air	Sensory parameters	20 min treatment significantly reduced flavour and overall acceptability scores (from 6.82 to 5.82)	Park and Ha (2015)
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Sensory parameters	NTP treatment for 5 min and longer significantly increased appearance, color and overall acceptance scores. No differences in flavour scores between treated and untreated samples	Puligundla et al. (2017)
Dried laver	Corona discharge plasma jet system; 20 kV; 58 kHz	Air	DPPH radical scavenging properties, TPC	No differences between treated and untreated products	Kim et al. (2015)
Fresh mackerel fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 1, 3 and 5 min	Air	Oxidation rate (peroxide value (PV), dienes, TBARS)	Significant increase in PV (5-fold) and in dienes (4-fold). Both time and voltage increase oxidation rate. No differences in TBARS.	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017)
Fresh Atlantic herring fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 5 min	Air	Oxidation rate (TBARS)	Significant increase in oxidation caused by NTP treatment with positive correlation between voltage and oxidation rate	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, and Rico (2017
Salmon nigiri and hosomaki	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; 5 min	Air	Oxidation rate (TBARS)	Significant increase in TBARS after NTP treatment, with slightly higher rates for 80 kV treatment	Kulawik et al. (2018)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Oxidation rate (TBARS)	Significant linear increase in TBARS after treatment	Choi et al. (2017)
Dried squid shreds	Corona discharge plasma jet system, 20 kV; 58 kHz; 1, 2 and 3 min	Air	Oxidation rate (TBARS, PV)	Significant increase in TBARS with treatment time correlated with increased oxidation.  No significant differences in PV between treated and untreated samples	Choi et al. (2016)
Dried filefish fillets	Not specified; treatment time 3, 5, 10 and 20 min	Air	Oxidation rate (TBARS)	Significant increase in TBARS after treatment, with oxidation rate increasing with treatment time	Park and Ha (2015)

(Continued)

Table 3. Continued.

Product	NTP parameters	Plasma working gas	Parameter	Main findings	References
Semi-dried Pacific saury	Corona discharge plasma jet system; 20 kV; 58 kHz; 3, 5, 7 and 10 min	Air	Oxidation rate (TBARS, PV, acid value (AV))	No significant changes in PV and AV between treated and untreated samples. Significant increase (by 2-fold) in TBARS after 5 min treatment and longer	Puligundla et al. (2017)
Fresh mackerel fillets	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; treatment time 1, 3 and 5 min	Air	Fatty acids composition	Significant differences in fatty acids composition between treated and untreated samples	Albertos, Martin-Diana, Cullen, Tiwari, Ojha, Bourke, Álvarez, et al. (2017)
Salmon nigiri and hosomaki	Dielectric barrier discharge system; 70 and 80 kV, 50 Hz; 5 min	Air	Fatty acids composition	No significant changes between treated and untreated samples	Kulawik et al. (2018)

NTP treatment was effectively used on semi dried Pacific saury (Cololabis seira), reducing microbial loads of aerobic, marine and colifrom bacteria as well as yeasts and molds and Staphylococcus spp. counts by 2-3 log cfu/g after 10 min treatment (Puligundla et al. 2017). The treatment did not affect moisture content, TVB-N, pH or water activity but it very distinctively changed color parameters, improving lightness, redness and yellowness of the sample which in turn significantly improved sensory scores for appearance color and overall acceptability. The treatment induced oxidation, increasing by 2-fold TBARS content, this change however did not affect the flavor sensory scores of the final product.

The above studies suggest that NTP could be an effective decontamination method for dried fish and seafood which does not reduce, or sometimes even improves the sensory quality of the final product. On the other hand, Park and Ha (2015) studied the effect of NTP on dried filefish fillets inoculated with Cladosporium cladosporioides Penicillium citrinum and observed that although cold plasma treatment for 20 min reduced the microbial loads, it has also significantly increased oxidation rate and significantly reduced flavour and overall appearance scores during sensory analysis.

The NTP treatment is more effective in improving the shelf-life of dried and semi-dried seafood than of its fresh counterparts reducing not only the microbial loads but also water activity of the samples without negatively affecting the sensory properties of the product. However the parameters of the treatment should be carefully designed for each type of treated product since longer treatments with high power can negatively affect the oxidation rates.

### Plasma activated water and wastewater treatment

NTP can be also used to create plasma activated water (PAW). PAW can be created through direct exposure with plasma discharge generated directly in water, or through indirect method, where plasma is generated in air and the formed ROS are transferred into the water. The latter is considered more effective in terms of energy efficiency (Ma et al. 2015). The indirect plasma treatment of water results in formation of various ROS in water, mainly H2O2 and nitrogen reactive species, such as  $NO_2^-$  and  $NO_3^-$ , as well

as metal ions, which provides antimicrobial effect through synergistic effect of induced oxidation and significant drop in pH (bellow 3) (Oehmigen et al. 2010, Chen et al. 2017). Those compounds can be present in PAW even for few days after plasma treatment, resulting in prolonged decontamination effect of suspended products (Traylor et al. 2011). On the other hand, pH seems to be the crucial parameter for the decontamination, since the treatment efficiency drops rapidly with increased pH of the PAW even when ROS and metal ions are present (Chen et al. 2017).

The efficiency of PAW has been tested on number of pathogens, effectively reducing the counts of E. coli, S. aureus, Hafnia alvei, Streptococcus mutans, Actinomyces viscous and Porphyromonas gingivalis (Traylor et al. 2011, Shen et al. 2016, Suwal et al. 2018, Ma et al. 2015, Kamgang-Youbi et al. 2008). It has also been effective in reducing microbial loads on food products effectively extending the shelf-life and reducing bacteria and fungi loads of Chinese bayberry and button mushrooms during storage (Ma et al. 2016, Xu et al. 2016). Therefore PAW could be applied within fish industry to treat water which is used for washing the fish during the basic processing steps such as gutting, filleting or skinning, since poor quality of water used during those fish processing steps can result in cross-contamination of the final product (Kirby et al. 2003).

The formation of nitrates in PAW leads to one more interesting application of cold plasma technology which is fish curing. The use of nitrates during curing process is usually applied to red meat products, to improve flavour and color as well as increase microbial stability, including prevention of growth of Clostridium botulinum (Gassara et al. 2016), however certain fish products, such as tunafish, sabrefish, salmon or shad are also cured (FDA 2017). The use of nitrate containing PAW can reduce or even eliminate the use of curing salt during curing process (Misra and Jo 2017), and through the process of plasma activated brine injection the antimicrobial effect of plasma treatment could be even more pronounced, although more research would be necessary to confirm this.

NTP could also be effectively used for the treatment of wastewater from fish industry, allowing for its reuse. The typical pollutants in wastewater from seafood industry include ammonia, chlorine, food additives, chemical

disinfectants, cleaners and aids, polychlorinated biphenyls or pathogenic bacteria including fecal coliforms (AMEC 2003). The amount of pollutants in wastewater is often characterized by two units: biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The first is the amount of oxygene dissolved in the effluent to degrade the organic material present in the wastewater by the aerobic bacteria while the latter is the measure of oxidizable pollutants in the effluent (Kim et al. 2000). Since NTP treatment results in formation of many ROS in PAW, it can replace other effluent treatment methods such as ozone or chlorine treatment. Many of the pollutants commonly associated with seafood industry wastewater, such as ammonia, phenols, chlorophenols, or benzoic acid have been shown to be completely degraded in wastewater by NTP treatment (Cheng et al. 2007, Malik et al. 2001). Moreover Patange et al. (2018) showed that NTP DBD system have effectively reduced the counts of E.coli, C. perfringens and E. faecalis in model dairy and meat industry effluent bellow the detection point, after 5 min treatment using 60, 70 and 80 kV. The authors also reported that higher fat content of the effluent resulted in lower decontamination efficiency, with longer treatment time needed to reduce bacteria loads bellow detection point. It is also worth mentioning that plasma treatment of wastewater is an cost effective method, since when air is used as an operating gas, the cost of operation of a industrial scale plasma device with power intake of 90 kWh would cost approx. 4.5\$/h. (Niemira 2012). On the other hand Patange et al. (2018) reported a slight increase in eco-toxicity of the plasma treated effluent, however the method is still more environmental friendly than chlorination (Malik et al. 2001).

The PAW has high potential to be used in almost all processing steps of seafood processing, from steps which include washing of seafood till wastewater purification. PAW allows to improve the microbiological quality of the fresh seafood without the disadvantage of increased oxidation observed during direct treatment of fresh seafood with NTP. The method has low operation costs and high efficiency. Therefore performing research which would study the effect of PAW used during each processing step on the microbial quality of the seafood and the effect of seafood wastewater purification with NTP on the purification efficiency and environmental toxicity seems crucial and the lack of such data is surprising. There is definitely need for more research on this subject in order to improve the chances of the technology being successfully transferred into seafood industry.

# Other uses of non-thermal plasma in fish and seafood

Although cold plasma have been mostly used as a decontamination method, recently there have been studies which show different possible applications of this method that could be potentially used within fish and seafood industry.

Cold plasma has recently gained attention as a possible method for reduction of immunoreactivity of several food allergens including almonds, soy or wheat (Chizoba Ekezie

et al. 2018) and have been shown to significantly reduce IgE binding to tropomyosin 36-kDa, a major shrimp allergen, when treated with NTP generated by DBD system at 30 kV and 60 Hz for 1, 3 and 5 min, with treatment time correlated with increased allergenicity reduction (Shriver 2011). Although more studies would be needed to confirm this in other fish and seafood, this show a potential new field of applications of cold plasma within fish and seafood industry, since fish and seafood are considered as two of the eight major food allergens (so called Big 8) responsible for 90% of all the food allergies (FDA 2004).

Another example of alternative potential use of NTP was studied by Zhang et al. (2014) who used cold plasma to improve grafting polymerization of molecularly imprinted membranes which in turn were effectively used for detection of five pyrethroid inseciticides (fenvalerate, deltamethrin, cypermethrin, cyfluthrin and bifenthrin) residues in fish flesh.

NTP have also been proposed as a technology which could be used to accelerate lipid oxidation of fish oil in a fast and reliable manner. The acceleration of lipid oxidation is often used to analyze the oxidation stability of food products. The improved oxidation acceleration of fish oil by NTP can provide more realistic spoilage characteristics than commonly used acceleration techniques based on increased temperature (Vandamme et al. 2015).

As can be seen the NTP can be used within many branches of seafood industries with applications not related to product decontamination. The wide spectrum of different effects the NTP has on the surrounding environment and product itself allows for using the technology in unconventional way when combined with out of the box thinking.

#### Conclusions

The data collected so far suggests that NTP treatment seems potent in reducing both overall microbial loads as well as various food pathogens, however the decontamination potential of NTP treatment is more pronounced in dried fish and seafood than in fresh fish. Although NTP treatment indeed induces the oxidation rate of treated fish and seafood, this does not necessary lead to decrease in sensory quality or shelf-life of the final products. There are studies suggesting the changes in protein structure and water distribution of the treated samples which should be further investigated to evaluate the potential impact the treatment can have on various fish and other seafood products. In case of fresh seafood the use of PAW could prove a powerful tool for maintaining a proper hygiene and reducing the microbial contamination of the final product without increasing the oxidation rate, however there is a lack of research which directly study the effect of plasma activated water on seafood quality. Additionally the NTP could be used for wastewater purification reducing the negative impact on the environment and reducing the costs of conventional wastewater management purification procedures.

Although there is still limited amount of research performed on NTP and seafood, the method has high potential



to be used in many fields within seafood industry. It allows treating products which cannot be treated with thermal processing methods, has low operating and investment costs and can be used in hurdle with other preservation or purification technologies. With the current state of knowledge the method could be recommended for the dried fish and other seafood producers, since the effectiveness of NTP within this field has been well documented.

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The authors declare that there is no interest or relationship, financial or otherwise that might be perceived as influencing an author's objectivity

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