

POTENTIAL OF OZONE UTILIZATION FOR REDUCTION OF PESTICIDE RESIDUE IN FOOD OF PLANT ORIGIN. A REVIEW

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ABSTRACT

Residues of plant protection products can be nowadays found in almost all samples of fruits as even if their application was carried out with respect to standards of Good Agricultural Practice. The intake of these compounds with food of plant origin may result in various disorders and diseases. Since the use of plant protection agents seems unavoidable, it is necessary to treat contaminated food material to eliminate or reduce residues content within food products. Ozone is utilized for elimination of biological and chemical contaminants in various environmental matrixes. Since its utilization in food industry has been permitted many experiments were conducted in order to determine its efficiency and side effects on food quality. The goal of this paper is to contribute to a discussion on the ozonization as a process leading to reduction of pesticide residues on plant surface.

Keywords: *pesticide residues, ozone, food processing*

STRESZCZENIE

Pozostałości środków ochrony roślin są wykrywane niemal we wszystkich próbkach owoców, nawet jeśli stosowane są zgodnie ze standardami Dobrej Praktyki Rolniczej. Pobieranie tych związków wraz z pożywieniem pochodzenia roślinnego może powodować różne zaburzenia i choroby. Ponieważ stosowanie tych środków wydaje się być nieuniknione należy poszukiwać metod usuwania bądź obniżania ich poziomu. Ozon jest używany do eliminacji zanieczyszczeń biologicznych i chemicznych w różnych matrycach środowiskowych. Odkąd zezwolono na stosowanie tego związku w przemyśle spożywczym przeprowadzono wiele eksperymentów w celu określenia jego skuteczności oraz skutków ubocznych. Celem niniejszego artykułu jest udział w dyskusji i przedstawienie publikacji dotyczących wykorzystania ozonu do ograniczenia poziomów pozostałości pestycydów na powierzchni roślin.

Słowa kluczowe: *pozostałości pestycydów, ozon, przetwarzanie żywności*

INTRODUCTION

One of the most important problems in production of food of plant origin is protection from pathogens and pests. Despite application of modern plant protection products in accordance with Good Agricultural Practice standards, it is nearly impossible to find any samples of some fruits (apple, raspberry and blackcurrant) without residues of their active ingredients [17].

Active ingredients of many pesticides seem to be very persistent and their residues decline very slowly. According to the studies made by *Gichner* detectable residues of some active ingredients present on the surface of grains and beans ranged from 16% up to 65% of the initial levels after 3–9 months of storage [11].

Half-lives of several organophosphorous insecticides (OPI) residues in products stored under typical condition (30 °C and 50% humidity) ranged from 2 weeks for dichlorvos (2,2-dichlorovinyl dimethyl phosphate - DDVP) up to 70 weeks for insecticides such as cyfluthrin and pirimiphos-methyl. Analogously, residues levels of malathion and pirimiphos-methyl in rape seed were reduced only slightly within 32 weeks of storage at 20 °C and in 50–70% relative humidity. At 30 °C residues of malathion decreased by 30–40% while pirimiphos-methyl residues remained constant [12].

Most of the unprocessed foods with high water content (such as berries) must be held in cold storage at temperature between 0–5 °C, or deep frozen (-10 to -20 °C), if they are intended for longer storage. The tests carried

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out on kiwifruit stored at 0 to 10 °C showed that after 3 months there was less than 20% decline of the initial residue levels of insecticides such as chlorpyrifos (OPI), diazinon (OPI), permethrin (pyrethroid insecticide; PI), phosmet (OPI), pirimiphos-methyl (OPI), or fungicides (iprodione or vinclozolin). Residue levels of benomyl, carbendazim, methyl thiophanate and thiabendazole in apples stored at 0–2 °C were also stable after 140–150 days where active ingredients were at 36–60% of the initial level [12].

The aim of this paper was to discuss the effect of ozone used as a disinfectant of stored fruits on the pesticides residues reduction.

REDUCTION OF RESIDUES BY WASHING PROCEDURES

Aside from food processing steps, methods which are commonly used for reduction of different impurities are based on washing with various agents.

For example, reduction of DDT residues with water wash varies from 20% for potatoes up to 91% for tomatoes [12]. Analogously, it was possible to reduce residue levels of other organochlorine pesticides (OCI) such as lindane (γ -hexachlorocyclohexane) and hexachlorobenzene (HCB) with water only. Observed decrease of pesticide residues was 18.1%, 20.7%, and 23.7%, respectively [20]. It should be underlined that these methods are able to remove pesticide residues by their transfer to washing solution. Such form of treatment contributes to increase of active ingredient concentrations in media such as air, water, or soil [21]. Efficiency of washing is dependent on several factors, such as location of residue within the fruit, time which passed since exposition to active ingredient and water solubility of particular residue. Also temperature and type of washing have an impact on this process. Introduction of detergents or additional agents and increase of solution temperature may considerably improve efficiency of the process [12]. *Zohir* observed that acidic agents i.e. citric acid, ascorbic acid, acetic acid were more successful in reduction of residual content of OCI contaminants than neutral (sodium chloride) or alkaline solution (sodium carbonate), as well as pure water [32]. Analogously, washing of potatoes with solutions of acetic acid and sodium chloride at different concentrations enabled reduction of OCI residues within ranges 18.2–40.1% for DDT, 18.8–65.3% for lindane and 23.7–59.7% for HCB. Also in that experimental work acidic solutions were more efficient for reduction of those insecticides. However, removal of organophosphorus insecticides residues such as dimethoate, pirimiphos-methyl and malathion was more effective with alkaline solutions [2, 20]. Reduction of fungicides such as myclobutanil (triazole), fenhexamid (hydroxyanilide) and boscalid (carboxamide) was possible within the range of 17.3–65.4% for washing procedures where water, sodium carbonate (Na_2CO_3), sodium hypochlorite (NaClO), glycerol and acetic acid were utilized [1].

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OZONE AS AN ALTERNATIVE TO REDUCE PESTICIDES RESIDUES ON PLANT FOOD PRODUCTS

Ozone is an allotrope form of oxygen which is a very strong oxidant ($E_0 = 2.07 \text{ V}$) that enables oxidation of many organic compounds. Up to date the use of ozone in food industry is limited to sanitizing of food products and storage facilities. *Barth et al.*, reported inhibition of fungal development on blackberry fruit stored in atmosphere enriched with 0.3 ppm ozone for 12 days [7]. *Tzortzakis et al.* [26–28] investigated development of microbial infection in clementines, grapes, tomatoes and plums in ozone enriched atmosphere. In that experiment ozone concentration of 0.1 ppm suppressed development of fungal infection for 13 days in comparison to the samples stored in atmosphere without ozone. Quality of tomatoes could also be maintained for a longer period of time in comparison to the control product. *Aguyo et al.*, observed that cyclic treatment of tomatoes with 4 ppm of gaseous ozone inhibited microbial infection of tomato fruits for 15 days. Such procedure resulted in overall better sensory quality of treated tomato fruits in comparison to the control fruits [4].

Efficiency of disinfection strongly depends on applied treatment technology. *Adams et al.*, reported that 500 ppm of chlorine solution enabled 88% reduction of bacteria, whereas 8 ppm of aqueous ozone solution was able to reduce 62% of microbial population. Chlorine and ozone washes were conducted at pH 7.6 for 30 min. In another experiment gaseous ozone at concentration of 40 ppm was used. Such treatment resulted in 47% reduction of population after exposition of microbes to gaseous ozone for 1h. Generally, highest reduction of pathogens can be achieved in different washing procedures where some portion of bacteria can be washed off [3]. With the introduction of ozone, control of pathogens such as fungi or bacteria can eliminate the necessity of fungicide application just before plant products would be placed in storage rooms. This fact alone can indirectly affect the levels of plant protection agents in stored food products.

Moreover, ozone can play also an active role in reduction of pesticide residues in stored products. This highly reactive agent has already been successfully applied for degradation of pesticide residues in diverse types of matrix. In the ozonation process main reaction, which is responsible for decomposition of chemical

contaminants in treated materials, is the ozonolysis of double bonds in unsaturated compounds. During this process ozone decomposes to pure oxygen, living no toxic byproducts. Those properties are the main reason why ozone has already been adapted in broad spectrum of environmental protection practices such as wastewater treatment [9, 15], soil remediation [6, 16] and other advanced oxidation processes.

Essentially, reduction of chemical contaminants in food products with ozone is based on two different procedures, i.e. washing with aqueous ozone solutions and treatment with ozone in gaseous phase. Both of them have advantages and disadvantages. Commonly fruits and vegetables are sprayed with aqueous solution of ozone or undergo passage through solution on an assembly line. Scheme of a typical installation produced by ozone solutions used for preparation of ozone solution in water is presented in Figure 1.

to double bonds [8]. Reactions between these radicals and organic contaminants have in general much faster reaction rates than reactions between ozone molecules and organic contaminants. On the other hand, they are less selective. This makes reactions of hydroxyl radical an optimal support for treatment procedures based on utilization of aqueous ozone in various advanced oxidation processes. On the other hand, due to the low selectivity of these radicals some undesired effects such as decrease of anthocyanins content [3, 19, 23], ascorbic acid [5, 24, 31] and color [22, 25] may occur. Proportion of direct and indirect oxidation pathways is affected by pH, UV light, ozone concentration and presence of radical scavengers [30].

Ozone potential for degradation of pesticide residues present on fruit surface have been proven by several studies. Even as low concentration as 0.25 ppm ozone in water enabled reduction of over 50% of residue levels

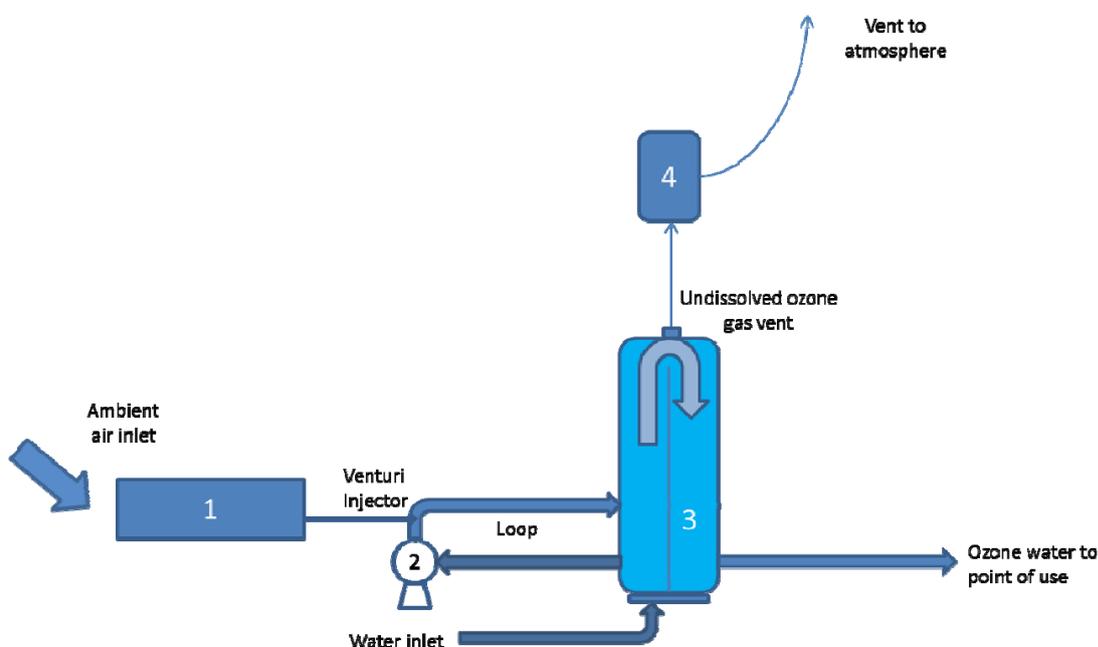


Figure 1. Scheme of installation for saturation of water with ozone; 1. ozone generator, 2. injection pump, 3. contact tank, 4. ozone destructor (from: <http://www.ozonesolutions.com/journal/category/food-industry>)

In contradiction to other popular agents, ozone, as mentioned above, decomposes to oxygen, leaving no trace of toxic or taste changing treatment byproducts. The use of ozone solution in water is possible due to its solubility in water, which is about 0.105 g in 100 cm³ at 0°C. If ozone is applied in aqueous solution the oxidation of contaminants can be based on direct oxidation by ozone molecules or on indirect oxidation by free radicals. A catalytic reaction of ozone with metal oxides may result in generation of other very strong oxidant ($E = 2.8$ V), a hydroxyl radical ($\cdot\text{OH}$). Hydroxyl radical reactions with organic compounds are based on hydrogen abstraction, or electrophilic addition

of substances such as azinphos-methyl (OFI), captan (phthalimide fungicide) and formetanate hydrochloride in fresh apples and their products. The ozonation process for removal of residues from treated material was more efficient at pH 4.5 than at 7 or 10.7, whereas temperature increase had low impact on this process [18].

The aqueous solution containing 2 ppm of ozone enabled 60% reduction of initial residue level of diazinon (OFI), parathion (OFI), methyl-parathion (OFI) and cypermethrin (PI) in vegetables [29].

Ozone is effective in much lower concentrations than other agents used for washing of food products. Hwang et al. [13] reported that a 3 ppm solution of ozone

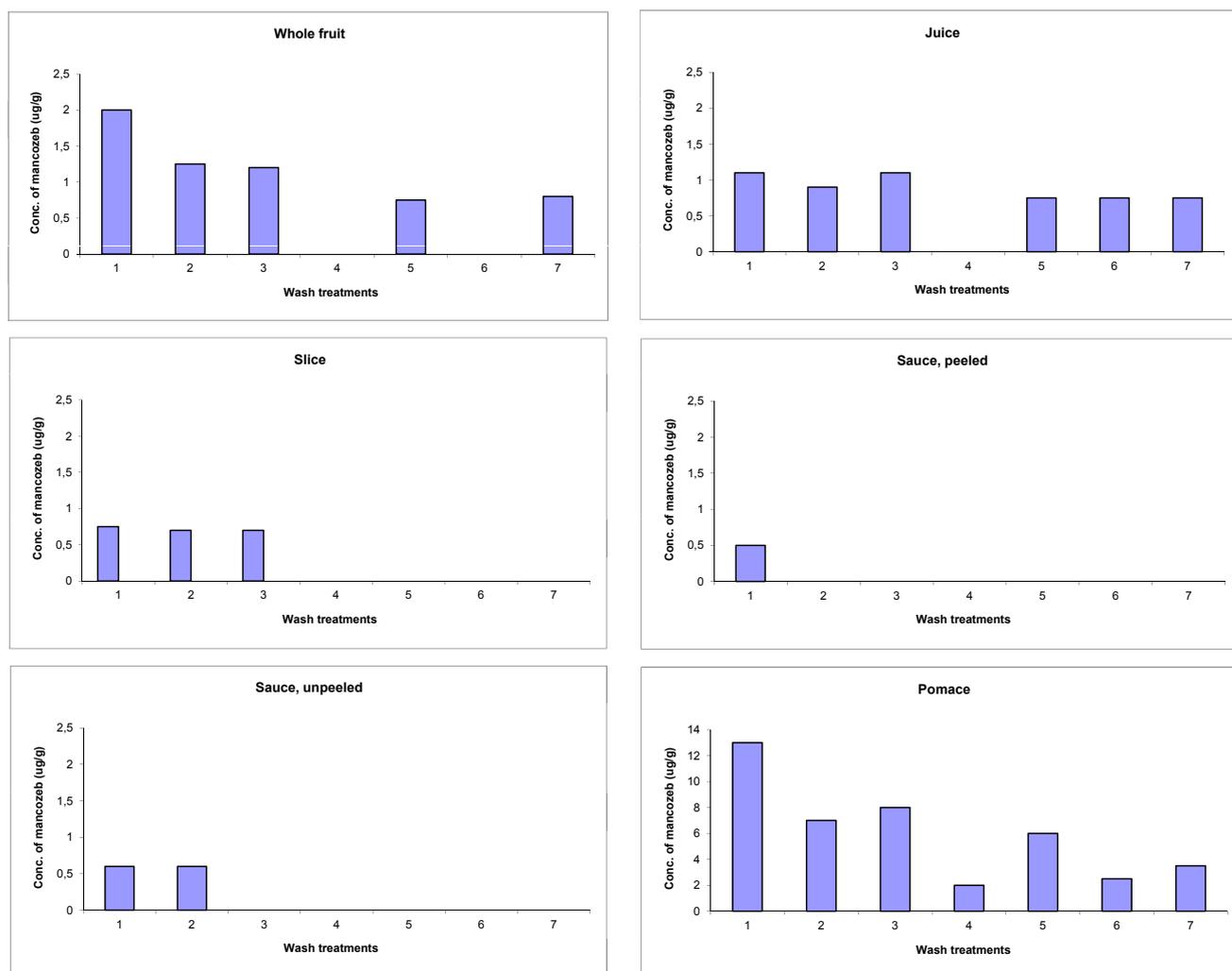


Figure 2. Concentration of mancozeb residues in apple and apple products after postharvest wash treatments. Wash treatments: 1- no wash, 2 - water wash, 3 - 50 ppm chlorine, 4 - 500 ppm chlorine, 5 - 10 ppm chlorine dioxide, 6 - 3 ppm ozone, 7 - 50 ppm HPA [13].

was as effective as 500 ppm of calcium hypochlorite ($\text{Ca}(\text{OCl})_2$), and more effective than 10 ppm of ClO_2 , i.e., for total degradation of mancozeb (dithiocarbamate fungicide; DTC) and ethylenethiourea (DTC toxic metabolite) in fresh apples and their products (see Figure 2).

Recently some experiments to optimize ozone treatment in aqueous solution have been made by *Ikeura et al.* [14]. As a result of use of a special generator, ozone micro bubbles (OMCB) could be generated, which were less than 50 μm in diameter. Ozone introduced in this form can reach higher concentration than in conventional systems where ozone milibubbles (OMLB) diameter is 2–3 mm. In that way efficiency of treatment with aqueous ozone solution can be enhanced (see Figure 3).

Despite the great ozone solubility and generation of hydroxyl radicals in aqueous solution, the use of ozone in gaseous form also has its benefits. Ozone in air is able to reach targeted compounds much faster due to the enhanced diffusion process in gaseous state in comparison to aqueous solution [10, 16]. Furthermore, as mentioned above half-life of ozone in gaseous solution is greater

than in aqueous solution, which makes it more stable and therefore active longer. Gaseous ozone has been already used for reduction of pesticide residues in the soil [6]. However, to our knowledge no studies on the gaseous ozone potential to reduce pesticide residues on fruits have been performed.

CONCLUSIONS

1. Although numerous research concerning sanitizing of food products with ozone were conducted, this review shows that there were only few studies concerning the use of ozone for reduction of pesticide residues in food of plant origin.
2. Ozone used in storage facilities was proven to inhibit development of microbial infection in food products. This fact alone is sufficient to reduce levels of fungicides in food products.
3. Ozone can also play an active role in cleaning of food products contaminated with pesticide residues.

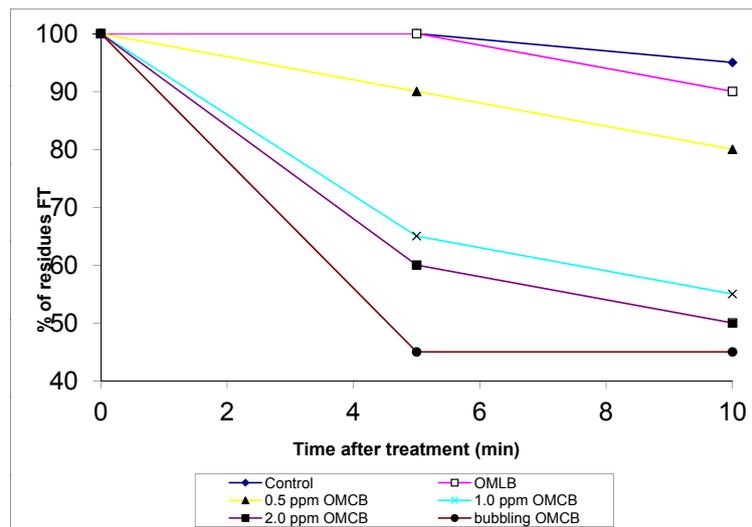


Figure 3. Changes in the residues of fenitrothion (OFI) in lettuce treated with the OMCB and OMLB solutions [14].

4. No evidence of research on degradation of pesticide residues with gaseous ozone in food products being conducted in the past was found.

REFERENCES

1. *Abdel Ghani S., Hanafi A., Nasr I.N.*: Non-toxic washing solutions for decreasing myclobutanil, enhexamid and boscalid residues in sweet pepper and cherry tomatoes. *Aust J Bas Appl Sci* 2010, 4, 3360–3365.
2. *Abou-Arab A.A.K.*: Behavior of pesticides in tomatoes during commercial and home preparation. *Food Chem* 1999, 65, 509–514.
3. *Adams C., Qiang Z., Demirkol O., Ercal N.*: Impact of food disinfection using ozone and other oxidants on the beneficial antioxidant content in vegetables. *IOA17th World Ozone Congress*. Strasburg 2005, VII. 2.2, 1–9.
4. *Aguayo E., Escalona V.H., Art'es F.*: Effect of cyclic exposure to ozone gas on physicochemical, sensorial and microbial quality of whole and sliced tomatoes. *Postharvest Biol Technol* 2006, 39, 169–177.
5. *Alothman M., Kaur B., Fazilah A., Bhat R., Karim A. A.*: Ozone-induced changes of antioxidant capacity of fresh-cut tropical fruits. *Innovative Food Sci Emerg Technol* 2010, 11, 666–671.
6. *Antos P., Józefczyk R., Kisala J., Balawejder M.*: Remediation of imidacloprid contaminated soil - comparison of two different reactors for the ozone treatment. In: *Risk factors of food chain: 11th international conference*, September 5-6, 2011 (Abstracts). Ed. *M. Dżugan, A. Pasternakiewicz*, University of Rzeszów, Pedagogical University in Krakow, Slovak University of Agriculture in Nitre, Ivonicz 2011, 13.
7. *Barth M.M., Zhou C., Mercier J., Payne F.A.*: Ozone storage effects on anthocyanin content and fungal growth in blackberries. *J Food Sci* 1995, 60, 1286–1288.
8. *Chiron S., Fernandez-Alba A., Rodriguez A, Garcia-Calvo E.*: Pesticide chemical oxidation: state of the art. *Water Res* 2000, 34, 2, 366-377.
9. *Esplugas S., Gimenez J., Contreras S., Pascual E., Rodriguez M.*: Comparison of different advanced oxidation processes for phenol degradation. *Water Res* 2002, 36, 1034–1042.
10. *Gana S., Lau E.V., Ng H.K.*: Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs). *J Hazard Mater* 2009, 172, 532–549.
11. *Gichner T.*: International Atomic Energy Agency, Studies of the magnitude and nature of pesticide residues in stored products, using radiotracer techniques. *Austria Sch.* 1990, 460, 143 Vienna.
12. *Holland P. T., Hamilton D., Ohlin B., Skidmore M. W.*: Effects of storage and processing on pesticide residues in plant products. *Pure Appl Chem.*, 1994, 66, 335–356.
13. *Hwang E.-S., Cash J.N., Zabik M.J.*: Degradation of mancozeb and ethylenethiourea in apples due to post-harvest treatments and processing. *J Food Sci* 2002, 67, 3295–3300.
14. *Ikeuraa H., Kobayashi F., Tamaki M.*: Removal of residual pesticides in vegetables using ozone microbubbles. *J Hazard Mater* 2011, 186, 956–959.
15. *Lafi W. K., Al-Qodah Z.*: Combined advanced oxidation and biological treatment processes for the removal of pesticides from aqueous solutions. *J Hazard Mater B* 2006, 137, 489–497.
16. *Masten S. J., Davies S. H. R.*: Efficiency of in situ ozonation for remediation of PAH contaminated soils. *Journal of Contam Hydrol* 1997, 28, 327–335.
17. *Nowacka A, Gusowski B, Waloreczyk S, Drożdżyński D., Wójcik A., Raczkowski M., Holdyńska A, Barylska E., Ziółkowski A., Chmielewska E., Rzeszutko U., Giza I., Łozowicka B., Kaczyński P., Rutkowska E., Szyrka E., Rupa J., Rogozińska K., Machowska A., Słowik-Borowiec M., Kuźmenko A., Szala J.*: Pozostałości środków ochrony roślin w płodach rolnych (Rok 2008). *Progress Plant Protect* 2009, 49, 1903-1917.
18. *Ong K.C., Cash J.N., Zabik M.J., Siddiq M., Jones A.L.*: Chlorine and ozone washes for pesticide removal from apples and processed apple source. *Food Chem* 1996, 55, 153–160.

19. *Perez A.G., Sanz C., Rios J.J., Olias R., and Olias J.M.*: Effects of ozone treatment on postharvest strawberry quality. *J Agr Food Chem* 1999, 47, 1652–1656.
20. *Soliman K.M.*: Changes in concentration of pesticide residues in potatoes during washing and home preparation. *Food Chem Toxicol* 2001, 29, 887–891.
21. *Street J.C.*: Methods of removal of pesticide residues. *Can Med Assoc J* 1969, 100, 154–160.
22. *Tiwari B.K., Muthukumarappan K., O'Donnell C.P., Cullen P.J.*: Modelling colour degradation of orange juice by ozone treatment using response surface methodology. *J Food Engin* 2008, 88, 553–560.
23. *Tiwari B.K., O'Donnell C.P., Cullen P.J.*: Effect of non thermal processing technologies on the anthocyanin content of fruit juices. *Trends Food Sci Technol* 2009, 20, 137–145.
24. *Tiwari B.K., O'Donnell C.P., Patras A., Brunton N., Cullen P.J.*: Effect of ozone processing on anthocyanins and ascorbic acid degradation of strawberry juice. *Food Chem* 2009, 113, 1119–1126.
25. *Tiwari B.K., O'Donnell C.P., Muthukumarappan K., Cullen P.J.*: Anthocyanin and colour degradation in ozone treated blackberry juice. *Innov Food Sci Emerg Technol* 2009, 10, 70–75.
26. *Tzortzakis N., Singleton I., Barnes J.*: Impact of low-level atmospheric ozone-enrichment on black spot and anthracnose rot of tomato fruit. *Postharvest Biol Technol* 2008, 47, 1–9.
27. *Tzortzakis N., Singleton I., Barnes J.*: Deployment of low-level ozone-enrichment for the preservation of chilled fresh produce. *Postharvest Biol Technol* 2007, 43, 261–270.
28. *Tzortzakis N., Borland A., Singleton I., Barnes J.*: Impact of atmospheric ozone-enrichment on quality-related attributes of tomato fruit. *Postharvest Biol Technol* 2007, 45, 317–325.
29. *Wu J.G., Luan T.G., Lan C.Y., Lo W.H., Chan G.Y.S.*: Efficacy evaluation of low-concentration of ozonated water in removal of residual diazinon, parathion, methyl-parathion and cypermethrin on vegetable. *J Food Engin* 2007, 79, 803–809.
30. *Young J. C., Zhu H., Zhou T.*: Degradation of trichothecene mycotoxins by aqueous ozone. *Food Chem Toxicol* 2006, 44, 417–424.
31. *Zhang L., Lu Z., Yu Z., Gao X.*: Preservation of fresh-cut celery by treatment of ozonated water. *Food Control* 2005, 16, 279–283.
32. *Zohair A.*: Behaviour of some organophosphorus and organochlorine pesticides in potatoes during soaking in different solutions. *Food Chem Toxicol* 2001, 39, 751–755.

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