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Study of Imidacloprid Degradation on Field-treated Tomatoes using Ozonation

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ABSTRACT

Field study was conducted with tomatoes (Solanum lycopersicum) to evaluate the effects of ozone treatment on imidacloprid. The effects of ozone treatment on the color and ascorbic acid content were evaluated. The ozonation treatments consisting of 20 mL of a 10 ppm solution were imposed for a period of 10 and 30 minutes. It resulted in 21 and 43 per cent reduction in the imidacloprid residue, when aaplied for 10 and 30 minutes respectively. The amount of degradation was directly related to the pesticide amount and the ozone treatment time. Increased imidacloprid degradation by ozonation yielded reduced toxicity. Significant increase in the degradation was observed due to increase in treatment timimg of ozonation for 15 and 60 minutes from 7% to 12.2%, respectively. The washing of field imidacloprid-treated with ozonated water reduced the pesticide residue significantly compared with washing with water. However, ozonation caused a significant reduction in the ascorbic acid content and had no effect on color in tomato samples.

Keywords: Daphnia magna, ozone, pesticide, residue, tomatoes.

INTRODUCTION

Pesticides are one of the strong tools to increase agricultural productions if used in efficient manner. More than 1000 active substances against pests are currently used worldwide. In addition, pesticide accumulation on agricultural products presents severe risks to public health because pesticides are toxic even at low concentrations (Ladislao, 2008). Pesticide residues and their fates in the environment also have important ecological effects. In many countries strict regulations are applied to organize pesticide residues on food products. At the international level, residue tolerances for pesticides are determined by the Codex. Many countries analyze both domestic and imported food products to determine if they have pesticide residues. Although pesticide residues in foods generally have minimal risk because of regulations, they sometimes have firm risks for the consumers. The major reasons for rejection of plant foods exported from Turkey to European Union countries in 2004 were pesticide and toxin residues followed by fungal and bacterial contamination (Delen *et al*., 2005).

Many treatments are applied to remove pesticides from food products and to minimize their health risks. Heat, steam, light, and acid or alkaline conditions are used to degrade or reduce pesticide residues. At the same time major reductions of residue levels result from their physical removal by peeling, cleaning or trimming of foods, such as vegetables, fruits, and meat (FAO, 2010). However, to degrade pesticides from aqueous solutions, some physicochemical techniques has been developed, such as Fenton oxidation (Hinacapie *et al*., 2005; Martin *et al*., 2009), electrochemical oxidation (Errami *et al*., 2012), UV radiation (Beketov *et al*., 2011), biological applications (Martin *et al*., 2009) and TiO_2 catalytic application (Sharma *et al*., 2008). Chemical oxidation appears to be a key technology for solving the pesticide problem. Ozonation is one of the most promising chemical oxidation techniques and has been used for pesticide degradation for a long time. Some studies have denmonstrated that high microbial inactivation rates can be obtained with both aqueous and gaseous ozone treatments (Hassenberg *et al*., 2008; Gabler *et al*., 2010), and ozone treatments can also decrease the level of pesticide residues in water (Jasim *et al*., 2006).

Ozone is an approved sanitizing agent that is being tested

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widely in the food industry for disinfection purposes. Because of its quick decomposition to oxygen, which decreases concerns about toxic residues, it has attracted interest in regards to food safety issues. On the contrary, ozone can also be responsible of some detrimental effects on product physiology and quality losses such as damage to color and antioxidant constituents, which are the result of its strong oxidizing activity (Vurma *et al.,* 2009). Imidacloprid (IMI, 1-[6-kloro-3-piridilmetil]-N-nitroimidazolidin-2-ilideneamin), a widely used pesticide and a member of the neonicotinoids, is used for pest control purposes around the world (Zeng and Wanga, 2010). IMI was first used in 1991 and has been increasingly used since then. It is believed that this increase is the result of marketing IMI as a neonicotinoid insecticide. Because IMI is the antagonist of the postsynaptic nicotinic acetylcholine receptor of agriculturally harmful insects, it can highly control these insects by disrupting their normal neural operations (Tomlin, 2003; Tomizawa and Casida, 2005). In recent years, contamination of aquatic ecosystems by pesticides has become a global problem. IMI also has the potential to contaminate surface and underground waters following use in agricultural products via streaming and filtration from soil (Gupta *et al.,* 2002). It is known that planktonic crustaceans are sensitive to neurotoxic chemicals similar to insects (Mark and Solbe, 1998), and there is a similar neurophysiology among macro crustaceans, large arthropods, spiders and insects. Because of this sensibility of daphnids, they are used as bioindicators to understand the water quality of soft water (Martins *et al.,* 2007). At the same time, daphnids are accepted as important species for understanding the safety level of pesticides in aquatic ecosystem and the toxicities of degradation products of pesticides (Sanchez-Bayo and Goka, 2006). After ozonation, degradation products are formed, but their chemical composition can not be exactly determined, and this appears to be the most crucial obstacle. For determining the effects of degradation products on human and animal health in vivo and in vitro toxicological tests are essential. The main objectives of this study were to determine the stability of imidacloprid (IMI) under various conditions and to determine the effects of ozone treatment on IMI removal, toxicity color and ascorbic acid content in tomatoes.

MATERIALS AND METHODS

Imidacloprid (IMI) was obtained from Agrobest (İzmir, Turkey) at 99% purity. Stock solution (20.000 mg/ L) and test solutions were freshly prepared by dissolving IMI (or stock solution) in ASTM Type 2 high-purity water (TKA Scientific, Niederelbert, Germany).

Ozonation apparatus and procedure

Ozone was produced from air by a corona discharge ozone generator (OG-20, Opal, Turkey) with a production capacity of 20 g/h of ozone. The pesticide solutions were ozonated in 50 mL Falcon test tubes or 250 mL glass bottles (Isolab, Boro 3.3, Wertheim, Germany) depending on the ozonated volume. The caps of tubes (or bottles) had a hole on the center to let tubing pass through. The tubing was connected to a stainless steel solvent inlet filter (10 μm pore size) from Fisher Scientific (Schwerte, Germany). The filter was kept at the bottom of the tube (or bottle) during the ozonation process to allow efficient ozone diffusion in the liquid phase. The caps also had 6- 8 other small holes around the center hole to allow the release of ozone. The ozone flow was adjusted to 600 mL/min with a flowmeter "Riteflow", size 2, (Bel-Art Products, Pequannock, USA). All ozonation processes was performed at 15 °C using a cooling water bath (Polyscience, USA). After ozonation was complete, the reaction was stopped by using 10 μL of 5.2 g /L difco neutralizing buffer (Cat. No. 236210, Becton, Dickinson and Sparks, USA). All experiments were conducted in triplicate in a fume hood.

Analysis of IMI

The concentration of IMI was measured at Ankara University, Food Engineering Department in 2011 by high performance liquid chromatography (HPLC). The Shimadzu (Japan) system consisted of a LCX-20AD pump, a SPD-M20A PDA detector, a DGU 20A5-E degasser, and a CTO-10ASVP column oven. The working temperature, injection volume and detection wavelength were 25 °C, 20 μL and 270 nm, respectively. A mixture of methanol: water (60:40) at a flow rate 0.5 mL /min was used as the mobile phase under isocratic conditions. An Inertsil (GL Sciences, Japan) ODS-3 column (C18, 5 μm, 250 mm × 4.6 mm) was used in the experiments. Samples were filtered through a 0.45 μm PTFE filter (Millipore, Millex-LCR). The reductions in pesticide contents were calculated from the reduction of peak areas after ozone treatments.

Toxicity tests

Deionized water from a Millipore Milli-Q ultrapure (Milli-DI, France) water system was used throughout the study, with the exception of the daphnid culture. The test organism *Daphnia magna*, obtained from the Kepez Aquaculture Research Institute (Antalya, Turkey), was introduced into 30 L aquariums with dechlorinated tap water, which served as holding tanks. Cultures were maintained and all experiments were run in an environmental chamber. The water temperature, dissolved oxygen, pH, and electrical conductivity were measured regularly in the laboratory; the temperature was 20.2 ± 1.3°C, and the photoperiod was 12:12 h light: dark. Dissolved oxygen levels and electrical conductivity in the holding tanks were 6 mg/L and 250 μS/cm respectively. The daphnids were maintained and fed *Scenedesmus sp.* daily, according to the animals' age: 3 × 106, 5 × 106, and 6 × 106 cells /day per individuals aged 0-7, 8-15 days, and older than 15 days, respectively. *D. magna* was cultured according to

the procedures outlined in ISO 6341 (Anonymous, 1996). All reagents were of analytical grade, and all laboratory glassware was soaked in 10 % HNO_3 for at least 48 h and rinsed three times with distilled water prior to use. For the toxicity tests, each 100 mL aliquot of a 250 mg/L IMI solution was ozonated for 15, 30 and 60 minutes. After the addition of a reaction stopper, toxicity testing was performed immediately. In this part of the study, toxicity testing was performed considering the data given in the literature in which LC_{50} is reported to be 85 mg/ L for *D. magna* in IMI (Tomlin, 2003). A total of 10 neonates (age <24 h) obtained from the original culture were exposed to 10 different concentrations of IMI (75, 80, 85, 90, 95, 100, 105, 110, 115 and 120 mg/L). Those different concentrations were tested three times with control groups under static non-renewal conditions in 100 mL of reconstituted water in 250 mL Erlenmeyer flasks. There was no feeding during the test. The toxicity was expressed using the median lethal concentration, that is, the dose required to kill half of the daphnid members during a 24 h period of LC_{50} exposure.

Imidacloprid applications in the field

Field trials were performed in a tomato field on the 85th km marker of Ankara-Beypazarı road. One parcel was used for IMI experiments, and another was used for controls. Each parcel had a 10 × 3= 30m^2 area. A commercial preparation of IMI, Efedor SC350 (Agrobest, Turkey) was used as an IMI source, having 350/L pure active ingredient, which is registered in Turkey to prevent whitefly on tomatoes at a 100 mL decare^{-1} dose. According to the technical guide for the insecticide, Efedor SC 350 was applied three times with 10 to 14 day intervals between applications. A pressurized portable backpack sprayer was used for pesticide application. A calibration process was run before IMI treatment. Exactly 10 L of water was measured and added in a sprayer receptacle, and the amount of sprayed water was determined to be 4 liters for the 30 m^2 parcels. According to the amount of consumed water and registered Efedor SC350 (100 mL/decare), 3 mL of pesticide was applied to the experiment parcel. Before every insecticide application, the calibration was repeated. Tomato samples were collected and brought to laboratory at day zero (after 3 hours of pesticide application) to determine the highest content level. A 2 kg tomato sample (at least eight mature tomatoes) was taken for each treatment from the control and experiment parcels according to the "systematic sampling" method (Anonymous, 2011). All of the experiments were also performed with controls in triplicate. For IMI removal experiments, the water and ozone treatment times were 5 minutes.

Determination of color and ascorbic acid in tomatoes

The color of the tomatoes was determined according to the Hunter L, a, b scale using a Minolta CR 300 colorimeter. After calibration of the colorimeter with its own plate, every tomato sample was measured four times, and the data were recorded. The b (redness/yellowness) values were taken into account to evaluate color difference. The determination of ascorbic acid in tomatoes was performed according to the method of Reyes *et al.* (2007) with a slight modification. The tomato samples from the blender (4 ± 0.001 g) were weighed in a plastic beaker, and 24 mL of a citric acid solution (3%) were added. The beaker was placed in an ice bath, and its contents were homogenized using an Ultraturrax homogenizer. The homogenate was filtered through a filter paper (Whatman No. 41) and the filtrate was centrifuged at 6 000 rpm for 10 min at 0 °C. The supernatant was cleaned up using solid-phase extraction cartridges (Phenomenex, Strata C18-E, 55 µm, 70 A, 100 mg, Torrance, CA, ABD) with the aid of an exhaust manifold. Before use, the cartridge was conditioned with 3 mL of methanol and then 3 mL of distilled water. The filtrate was subjected to high performance liquid chromatography (HPLC). The Agilent 1100 instrument consisted of a computer-controlled system with *ChemStation LC3D*. Other accessories included a DAD detector (242 nm), and a Thermo Scientific RP C-18 column, (250 × 4.6 mm, 5 µm). The column temperature, injection volume and flow rates were 25 °C, 20 µL and 0.5 mL/min, respectively. Ascorbic acid was separated isocratically using a mobile phase of 2% potassium dihydrogen phosphate solution (pH 2.4 adjusted with o-phosphoric acid). A stock solution of ascorbic acid (500 mg/L) was prepared by dissolving L-ascorbic acid (from Sigma-Aldrich) in a 3% citric acid solution. Standard solutions (25, 50, 100 and 250 mg/ L) were prepared using appropriate dilutions of the stock solution with the citric acid solution and were injected into the HPLC system to construct calibration curves. In the HPLC system, an ascorbic acid calibration curve was generated, and a regression coefficient $R^2 = 0.99$ was determined. In addition, for use in calculations, the amount of dry substance in the tomatoes was determined using a refractometer and was found to be 5.3 brix.The amount of ascorbic acid in the samples was calculated using an ascorbic acid calibration curve.

Statistical analysis

Experimental results were expressed as the means ± standard errors. Analysis of variance was performed with one-way ANOVA using SPSS for *Windows* (ver. 10.1, USA). Significant differences between the means were determined by Duncan's multiple range tests. Differences were considered significant at $p < 0.05$. All of the experiments were performed in triplicate.

RESULTS AND DISCUSSION

Stability tests were performed to evaluate the self-degradation of IMI without any treatment and IMI treated with ozone (temperature, humidity, light, etc.). Initially, a simple stability

test was performed to determine if self-degradation occurs with ozonated and non-ozonated IMI solutions during storage. These tests were also performed with living *D. magna* cultures and sometimes toxicity tests cannot be performed immediately after ozonation, depending on the live number of culture. Therefore, this information was needed.

Stability of IMI

To reveal the self-degradation of IMI during storage, basic stability tests were performed. A 10 mg/ LIMI solution was stored at different temperatures for 3 days, and the results are shown in Table 1.

Table 1: Stability of Imidacloprid (IMI) (10 mg/ L) at +4ºC, -18ºC and +22 ± 2ºC

Storage temperature ºC	Concentration (mg/ L)		
	Fresh soln.*	after 24 hours	after 72 hours
+22 ± 2 (Room temp.)	10^{Aa}	8.26 ± 0.20 ^{Ab}	6.80 ± 0.05 ^{Ac}
+4	10^{Aa}	8.74 ± 0.22 ^{Bb}	6.80 ± 0.15 ^{Ac}
18	10^{Aa}	9.14 ± 0.26 ^{Ca}	7.13 ± 0.07 ^{Bb}

*Different capital letters in the same column or different small letters in the same row indicate a significant difference ($p < 0.05$).

The concentration of the IMI solution varied significantly ($p < 0.05$) depending on the temperature and time. Therefore, it can be concluded that IMI was not stable during storage, even when frozen. Therefore, only a freshly prepared IMI solution was used for following experiments.

Stability of ozonated IMI

Because ozonated samples were also used for the toxicity tests, information about the stability of ozonated and frozen stored IMI was needed. Therefore, a 250 mg/L IMI solution was ozonated for 30 minutes and, divided into 4 bottles and three of bottles were kept in a freezer (18ºC). The IMI content was determined every day for three days (Table 2).

Table 2: Stability of ozonated Imidacloprid (IMI) (250 mg/ L, 20 mL) at 18ºC

Duration (day)	Concentration (mg/L)
0	219.54 ^{A}
1	213.94 ^{B}
2	204.86 ^{C}
3	192.82 ^{D}

*Different letters in the same column indicate a significant difference ($p < 0.05$).

According to the results in Table 2, it can be concluded that IMI was not stable even if it was frozen. Therefore, all of the toxicity tests were performed using only freshly prepared and ozonated solutions.

The necessity of the use of neutralizer for ozonated IMI

To determine if ozone is still effective after blocking gas flow for IMI degradation, a small experiment was performed. After ozonation of two test tubes containing 10 mL of 10 mg/L IMI solution, 10 mL of difco neutralizing buffer was added to one of the test tubes, and the IMI concentration was determined after 3 minutes. The neutralizer added and not-added samples contained 8.164 mg/L and 7.172 mg/L ^{IMI}, respectively. This difference ($p = 0.014$) was significant; therefore, neutralizing buffer was always used in the following experiments.

Removal of IMI with ozone treatment

To reveal the effects of treatment time on IMI degradation, 20 mL of 100 mg/L solution was ozonated for 10, 15 and 30 minutes. The results indicate that IMI can be degraded by using ozone. Increased treatment time resulted in increased IMI degradation, and the limiting factor when ozone is used for removing IMI on fruits or vegetables is the effects of ozone on other quality parameters. Another experiment was performed to understand the effects of ozone treatment on IMI degradation. In this case, in addition to treatment time, the treated volume of the IMI solution was also considered. The results are shown in Table 3.

Table 3: Degradation of Imidacloprid (IMI) (250 mg/L) by ozone treatment

Ozonated volume (mL)	20		100		200	
Ozonation time (min)	10	20	20	30	20	30
Reduction (%)	13.3 ± 2.81	22.4 ± 0.33	12.9 ± 0.33	12.9 ± 1.37	6.7 ± 0.30	8.1 ± 0.80

As seen in Table 3, an increased treatment time and a decreased volume (i.e. less IMI) resulted in increased IMI degradation, as expected. To clarify the results, another simple experiment was performed. In this case, 20 mL of an almost never used 1000 mg/L IMI solution was ozonated for 10 minutes. In this case, the reduction rate was found to be 12%, whereas it was 21% for the 10 mg/L. Lastly, another trial was performed to determine the effects of treatment time on IMI degradation. An IMI solution was prepared at 10 mg/L with a volume of 20 mL. The results are shown in Table 4.

Table 4: Effects of ozonation time on the degradation of Imidacloprid (IMI) (10 mg/L, 20 mL)

Ozonation time (min)	Reduction (%*)
2	5.3 ± 0.07^{A}
5	14 ± 0.08^{B}
6	16.4 ± 0.06^{B}
10	21 ± 0.12^{BC}
15	23 ± 0.07^{C}
20	30 ± 0.09^{D}
30	43 ± 0.46^{E}

*Different letters in the same column indicate a significant difference ($p < 0.05$).

As seen in Table 4, the IMI decomposition was related to the amount of applied ozone. The amount of degradation was directly related to the pesticide amount and the ozone treatment time (R^2 = 0. 96).

Effect of removal of IMI by ozone on toxicity

Before the toxicity experiments, the acute toxic effect (LC_{50} value) of imidacloprid was found to be 85 mg/L for *D. magna* according to the literature (Tomlin, 2003). On the basis of the published data mentioned above and the results of our preliminary experiments, the working concentrations were chosen to be 75, 80, 85, 90, 95, 100, 105, 110, 115 and 120 mg/L. The results were evaluated after 48 hours (Table 5).

Table 5: Effect of ozonation time on the toxicity of *Daphnia magna* (250 mg/L, 100 mL)

Ozonation time (min)	Reduction IMI (%)	LC50 value (mg/L)
Control	0.0	83.0
15	7.1	99.4
30	12.2	105.4
60	39.0	118.4

The LC_{50} value was found to be 82.964 (80.603 - 85.135) mg/L for the non-ozonated IMI solution. These data were in accordance with Tomlin (2003) and Fossen (2006) (85 mg/L). In the case of the ozonated IMI solution, the LC_{50} value is increased from 99.4 to 118.4 mg/L after 15 and 60 min. of ozonation respectively. This finding indicates that the increased ozonation time reduces the IMI toxicity, which is related to the degradation of IMI (Tables 3 & 4).

Effects of ozonation on field-grown tomatoes

Before evaluation of the ozone treatment, we examined whether IMI treatment alone had any effect on the color of the tomatoes (Table 6). IMI treatment resulted in a 7.4 ± 3.2% reduction in the a/b value.This result and the reduced a value may be attributed to the oxidative effect of IMI on the carotenoids in tomatoes.

As seen in Table 6, ozone treatment resulted in only a limited reduction of the a/b value. Malone (2003) reported no significant reduction of color change of tomatoes, Skog and Chu (2001) reported significantly less color change of broccoli from green to yellow after ozonation. Conversely, Badiani *et al.*, (1996) has reported that ozonation caused significant color changes on the surface of peaches. Following the color analyses, the IMI residues on the tomatoes were determined. According to the results, the treatment (for 5 min) of IMI containing tomatoes with ozonated or non-ozonated water resulted in a 40.88 ± 3.43 and 32.63 ± 2.61% reduction, respectively, indicating a significant difference ($p < 0.05$). Both results could be considered sufficient because of the high water solubility of IMI. However, to achieve better IMI removal, ozone treatment would be beneficial. Lin *et al.* (2012) reported that the removal rate (80%) of cypermethrin from tea leaves by O_3/UV/TiO_2 treatment was significantly higher than that achieved by water rinsing ($p < 0.05$), and this treatment was especially effective for the removal of insoluble pesticides. Another study supporting this idea, that of Kusvuran *et al.* (2012), examined the removal of chlorpyrifos ethyl, tetradifon and chlorothalonil pesticide residues from lemons, oranges and grapefruits by ozonation. The researchers found that washing the lemons, oranges and grapefruits with tap water was not as effective as ozonation in the removal of residual pesticides, and ozone treatment has a great potential for removal of residual pesticides from these fruits. This is an expected result because chlorpyrifos ethyl, tetradifon and chlorothalonil pesticides have low water solubility. Following the color analysis, the samples were subjected to an ascorbic acid assay. The results are shown in table 7.

Table 6: Effects of Imidacloprid (IMI) and wash treatments on tomato color

Treatments	L	a	b	a/b	Reduction (%) (a/b)*
Control parcel					
Tomatoes without any wash treatment	41.48±3.0	32.38±2.7	30.10±3.9	1.08^{A}	-
Ozonation for 1 min	40.95±2.2	30.02±3.0	29.82±4.1	1.00^{AB}	$7.4±5.1^{A}$
Ozonation for 2 min	41.36±2.3	32.36±3.1	33.40±3.5	0.97^{B}	$10.2±2.0^{B}$
Ozonation for 5 min	40.83±3.1	31.75±2.9	32.54±3.5	0.97^{B}	$10.2±2.7^{B}$
IMI treated parcel					
Control	37.0±2.6	30.70±2.7	30.60±2.5	1.00^{C}	-
Ozonation for 5 min	41.24±2.9	32.35±3.2	33.70±4.0	0.96^{C}	$4.0±1.6^{C}$
Soaking in water for 5 min	42.18±3.0	30.22±3.2	30.57±3.9	0.99^{C}	$1.0±0.7^{D}$

*Different letters in the same column indicate a significant difference ($p < 0.05$).

Table 7: Variances in ascorbic acid content in field IMI-treated tomatoes

Treatment	Ascorbic acid (mg/kg)*	Ascorbic acid (mg/ kg DM)	Reduction %*
Control parcel			
Tomatoes without any treatment wash treatment	99.4 ± 3.5^{A}	1875.5 ± 34.9	-
Ozonation for 1 min	80.64 ± 3.2^{B}	1521.5 ± 38.6	18.9 ± 0.6^{A}
Ozonation for 2 min	69.95 ± 2.6^{C}	1314.2 ± 49.1	29.9 ± 2.6^{B}
Ozonation for 5 min	67.62 ± 2.1^{C}	1275.8 ± 40.2	32.0 ± 2.1^{B}
IMI			
Control	96.53 ± 2.7^{D}	1821.3 ± 42.6	-
Ozonation for 5 min	57.26 ± 3.8^{E}	1080.4 ± 44.2	40.7 ± 2.5^{C}
Soaking in water for 5 min	69.02 ± 3.4^{F}	1302.3 ± 40.2	28.5 ± 2.3^{D}

*Different letters in the same column indicate a significant difference ($p < 0.05$)

The loss of ascorbic acid in tomatoes subjected to IMI treatment was limited when compared to that of untreated tomatoes. Even if the reason for this loss is not understood clearly, it is believed that one or more component of the pesticide's structure caused oxidation. The results revealed that the loss of ascorbic acid was directly proportional to the ozonation time of the pesticide-treated tomatoes. In addition, ascorbic acid loss was observed when tomatoes were soaked in water, because of the high solubility of ascorbic acid in water. Generally, washing vegetables in ozonated water results in 10-22% more ascorbic acid than washing in non-ozonated water. Zhang *et al*. (2005) reported that there was no significant difference between ascorbic acid contents of celery samples treated and non-treated with ozonated water.

CONCLUSION

Present study reveals that Imidacloprid (IMI) can be degraded to a desired level, resulting in decreased toxicity. Ozonation resulted in a significant decrease in the IMI content on the field-treated tomatoes without any significant loss of color. This might be due to of the high water solubility and oxidizability of ascorbic acid, it can be easily reduced; therefore, a sufficient level of caution should be exercised when using ozonation.

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