

## Investigation of Changes Against Time in the Artificial Gastric Liquid Medium of Pesticide Active Substances

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**ABSTRACT:** In this study, grown tomato samples were examined changes of pesticide active substances by two different methods in the artificial gastric liquid (AGL) medium prepared. In the first method, Trifloxystrobin and Imidacloprid pesticide active substances were sprayed on the tomato samples before the harvest period. Time-dependent change of the active substance of Trifloxystrobin; although initially 83.17 ng g<sup>-1</sup>, it was determined as 24.71 ng g<sup>-1</sup> in 240 min. The concentration of this active substance was determined that decreased with time and the % change was 70.29. While Imidacloprid active substance initially was 10.20 ng g<sup>-1</sup>, it was determined as 10.32 ng g<sup>-1</sup> at 240 min. It was determined that this active substance did not change between the first and the last concentration depending on the time. In the second method, 75 pesticide active substances were spiked to the tomato sample and the time-dependent change in the AGL medium was examined. The concentration of 10 active substances that above 70% of the change rate was determined that there was a statistical decrease depending on the time % changes in the range between 0-240 min. The concentration of 30 active substances in below 70% of the change rate was determined that did not a statistical decrease as depending on time. however, % changes were observed that there was a certain thought at different rates between the first and the last concentration after 240 min. The last 15 active substances 240 min concentrations were determined that increased of % changes compared to 0 min.

**Keywords:** Pesticide, tomato, LC-MS/MS, GC-MS/MS, AGL medium

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## INTRODUCTION

Fruits and vegetables create an important part of our daily diet. In order for the fruits and vegetables consumed to be useful, they should not contain any pesticide residues or are below the specified limits (Elmastas, 2018). Pesticides are known as agrochemicals used to, prevent, spray, or destroy harmful organisms and substances, growth, and development of the plant (Wu et al., 2019). Pesticides according to their chemical structures and functional groups are classified into various forms including organochlorine, organophosphorus, and carbamate. The most well-known among organochlorinated pesticides are Chlordane, Heptachlor and, Dichlorodiphenyltrichloroethane (DDT). The most known organophosphated pesticides are Chlorpyrifos, Diazinon, Malathion, and, Parathion. The most commonly known carbamate pesticides are Aldicarb, Carbaryl, Carbofuran. Also, some pesticides used as insecticides are Acetamiprid, Chlorpyrifos, Dieldrin, Heptenophos, Imidacloprid, Malathion, and Pirimicarb. Some pesticides used as protective fungicides are Azoxystrobin, Boscalid, Difenconazole, Trifloxystrobin, and Tebuconazole (Elmastas, 2018).

The history of pesticides known that used sulfur dust for insect controls by people in ancient Mesopotamia around 2500 BC. Although the use of pesticides can improve the quality and quantity of crops, pesticide residues in crops are generally harmful to humans. For this reason, many international organizations have regulated the maximum residue limits (MRL) in crops (Wu et al., 2019). These organizations are WHO, EC 2005, USDA, CODEX, CAC, HSE, and EFSA (Elmastas, 2018; Algharibeh and AlFararjeh, 2019; Jara and Winter, 2019). In our country, MRL is determined by the Ministry of Food, Agriculture, and Livestock (Elmastas, 2018). MRL value of pesticides commonly used in the European Union (EU) agricultural products is determined as 0.01 mg kg<sup>-1</sup> (Wu et al., 2019).

Despite benefits in agricultural areas of pesticides, it is known that it has had dangerous effects recently (Wei et al., 2018). In the release to nature of pesticides and consumption of food products contaminated with pesticides various health problems such as headaches, flu, skin rash, blurred vision, especially neurological and behavioral disorders in children, serious poisoning, blindness, genetic mutations, various types of cancer, birth defects, reproductive disorders, genotoxicity, carcinogenesis, cardiovascular diseases, endocrinological disorders in humans and animals, and even causes death (Arias et al., 2013; Hou et al., 2018; Calvo et al., 2019; Ersoy et al., 2019; Farajzadeh et al., 2019). Pesticides are not only toxic to the environment and human health. They are also known phytotoxic because of reactive oxygen species (ROS), lipid peroxidation, protein damage, and cause oxidative stress through DNA breaks (Hou et al., 2018). One of the most important negative effects of pesticides gives the long-term potential damage to the health of practitioners and other staff exposed to pesticides, as well as varying acute-grade injury. Studies estimate that 2-3 people are poisoned by pesticides every minute, and about 20.000 agricultural workers die from pesticide poisoning every year (An et al., 2018).

Various analysis techniques are used to identify pesticide residues (Song et al., 2019). Some of those are gas chromatography (GC), liquid chromatography (LC) (Farajzadeh et al., 2019), gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass (LC-MS) (Song et al., 2019), liquid chromatography-tandem mass spectrometry (LC-MS/MS) (Algharibeh and AlFararjeh, 2019), GC-MS/MS (Lehotay, 2019), ultraviolet (UV) and fluorescent (FLD) detectors equipped with LC (Kapsi et al., 2019).

In this study, the time-dependent change of pesticide active substances in two different medium conditions in the AGL medium prepared grown tomato samples was examined. In the first medium, Trifloxystrobin and Imidacloprid active substances were sprayed on tomato samples before harvest. The time-dependent changes in the prepared AGL medium of these two active substances in the tomato

samples were examined. In the 2nd medium, some pesticide active substances were spiked to the tomato sample. The behaviors against time in the AGL of pesticide active substance spiked on tomato samples were investigated. In the literature, there is no information about monitoring the behavior of pesticide active substances in AGL. Thanks to this study, the knowledge of how the pesticide active substances change in the AGL medium will offer to contribute to the literature. Again, thanks to this study, it will be a guide in terms of working and evaluation in different artificial medium liquids.

## MATERIAL AND METHODS

### Herbal Material

Tomato sample was grown in the Research and Application field of Dicle University Faculty of Agriculture, Department of Horticulture. Tomato samples grown before harvesting time were done spraying process with Trifloxystrobin and Imidacloprid active substance and used in experimental studies.

### Chemicals and Reagents

Pesticide standards (Dr. Ehrenstorfer GmbH), Pepsin, and Hydrochloric acid (Sigma Aldrich, Germany) were provided commercially. Preparation of AGL; 6 g Pepsin 1% serum physiological solution taken and 4 M 2.5% HCl solution added on it. Then the final volume of the mixture was completed to 1000 ml. The pH of the AGL medium was adjusted to 1.2 (Galia et al., 1998).

### Extraction of Samples

The extraction of the samples was done according to the AOAC 2007.01 (International Official Methods of Analysis) method. Extraction procedures were carried out as follows.

15 g of tomato sample was weighed and homogenized with the help of a homogenizer. The obtained 15 g of the homogeneous mixture was taken into a 50 mL centrifuge tube and 15 mL of acetonitrile solution containing 1% acetic acid on it was added. Later the mix 1 min mixed with the vortex. Then, the salt mixture prepared from a mixture of 6 g magnesium sulfate and 1.5 g sodium acetate was added to the tube and the mixture was shaken for 1 min with the vortex. The mixture was then centrifuged at 4000 rpm for 5 min. Then, 8 mL of the upper phase was taken and placed in the centrifuge tube, and the salt mixture prepared from a mixture of 0.4 g primer amine and 1.2 g magnesium sulfate was added to the tube. The mixture was shaken by the vortex for 1 min and centrifuged at 4000 rpm for 5 min. Then, the upper phase was taken and filtered through a 0.45 µm filter and taken into the vial.

### Pesticide Active Substances in Tomato Sample

A total of 75 pesticide active substances were spiked into the tomato sample. 60 of these active substances were analyzed by LC-MS/MS and 15 by GC-MS/MS device.

### Experimental Design

AGL designed two different media studies. The tomato sample which is found Trifloxystrobin and Imidacloprid pesticide active substances in the 1st the designed medium was left in the AGL medium. It was then shaken continuously at 37 °C in a shaking water bath. At the time of release, it was accepted as 0 min, and samples were taken from the medium and analyzed. The same procedures repeated every half hour and 240 min analyzes continued to be made. In the second medium, some pesticide active substances were spiked to the tomato sample. They were spiked to the tomato sample with a final concentration of 100 ppb and the AGL was added and their behavior towards time was examined.

## Pesticide Residue Analysis in Samples

The pesticide active substances in the tomato sample were analyzed with Shimadzu GC-MS-TQ8040 and Agilent LC-MS/MS-6460 brand devices. Optimization studies were carried out on both the devices using the main stock standards prepared from 222 pesticide standards. The optimum conditions of both devices are given in Tables 1. analyzes were performed on both devices with 3 replicates of the samples in the vial under the optimum operating conditions and pesticide residues in the samples were determined using the data and library in the device.

**Table 1.** LC-MS/MS and GC-MS/MS device operating conditions

LC-MS/MS operating conditions					GC-MS/MS operating conditions			
LC-MS/MS		Agilent 6460			GC-MS/MS		Shimadzu TQ 8040	
Mobile Phase A	5 mM Ammonium format + % 0,1 Formic acid + 1000 mL Water				Column	Rxi-5SilMS (15 m x 0.25 mm x 0.25 um)		
Mobile Phase B	Pure methanol				Injection Volume	2 µl		
Column	Poroshell 120 SB-C18, (3.0 x 100 mm 2 microns)				Pressure	63 kpa		
Injection Volume	2 µl				Flow rate	1.85 mL min <sup>-1</sup>		
Flow	0.5 mL min <sup>-1</sup>				Carrier gas	Helium		
Run Time	12 min.				Run Time	18.81 min.		
Pump Gradient Program					The Column Oven	90 °C		
No value	Time (min.)	%Mobile Phase A	%Mobile Phase B	Flow rate ml/min	Injection temperature	250 °C		
No value	00:00	80	20	0.5	Column temperature Program			
No value	00:20	80	20	0.5	Start	Increase speed (C/min.)	Temperature	Standby time (min.)
No value	1:50	30	70	0.5	1	0	90	1
No value	6:00	5	95	0.5	2	30	150	0
No value	7:50	5	95	0.5	3	7	200	0
No value	7:60	80	20	0.5	4	15	300	2
No value	11:00	80	20	0.5				
No value	12:00	80	20	0.5				

## RESULTS AND DISCUSSION

The properties of Trifloxystrobin and Imidacloprid active substance found in tomato samples are given in table 2.

**Table 2.** Properties of Imidacloprid and Trifloxystrobin active substances

No	Active Substances	Chemical Class	Molecular Formula
1	Trifloxystrobin	Strobilurin	C <sub>20</sub> H <sub>19</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub>
2	Imidacloprid	Neonicotinoid	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>2</sub>

Türköz et al. in a study did in (2014); Between 2010 and 2012, they made pesticide active substance analysis using 1423 fresh fruit (Apple, grapes, apricot, banana, carrot, cherry, kiwi, lemon, orange, peach, pear, plum, pomegranate, strawberry and tangerine), and vegetable samples (Tomato, eggplant, pepper, cucumber, beans, cabbage, cauliflower, leek, lettuce, mushroom, onion, potato, purslane, arugula, and pumpkin). The most common active substances, they stated that Acetamiprid, Chlorpyrifos, Azoxystrobin, Boscalid, Carbendazim, Imidacloprid, Pyridaben, and Triadimenol (Türköz et al., 2014).

Diop et al. in (2016), in the study of determining pesticide residues in a total of 175 vegetable samples (31 cabbage, 88 lettuce, 57 tomatoes) in four different periods in the Niayes region of Senegal indicated that 65% of tomato samples 71% of lettuce samples and 93% of cabbage samples contained

one or more pesticide residues. The detected DDT, Dicofol, Chlorpyrifos, Dimethoate and  $\lambda$ -cyhalothrin pesticide active substances reported that each sample group was dominant at least 35% (Diop et al., 2016).

Zengin and Karaca, in a study made in (2017); between 2015 and 2016, Turkey's Usak province the pesticide active substance analysis in the 60 piece tomato samples collected in the greenhouse areas was done using LC/MS/MS and GC/MS devices. In the calculation of pesticide residue amount in 25 piece tomato samples collected in 2015; Imidacloprid and Acetamiprid were determined to be between 0.021-0.099 and 0.022-0.078 mg kg<sup>-1</sup>, respectively. According to the analysis results of 35 piece tomato samples collected in 2016, the active substances of Trifloxystrobin, Imidacloprid, and Azoxystrobin were determined to be between 0.011, 0.015-0.336 and 0.045-0.061 mg kg<sup>-1</sup>, respectively (Zengin and Karaca, 2017).

In the 1st medium designed, the results of the AGL medium of pesticide active substances in the tomato sample are given in table 3.

**Table 3.** Time-dependent change of pesticide active substance in the tomato sample in AGL.

Time (min.)	Trifloxystrobin (ng g <sup>-1</sup> )	Imidacloprid (ng g <sup>-1</sup> )
0	83.17	10.20
30	75.16	10.02
60	57.99	10.03
90	54.16	10.15
120	43.65	10.18
150	37.67	10.01
180	32.93	10.02
210	32.24	10.25
240	24.71	10.32
%Change	<b>70.29</b>	<b>-1.18</b>

When the active substances are evaluated according to the above results and chemical properties; While the active substance of trifloxystrobin was 83.18 ng g<sup>-1</sup> in 0 min. It decreased in the following times and was determined as 24.71 ng g<sup>-1</sup> in 240 min. Change in concentration depending on time was observed as 70.29%. It is possible to talk mention a decrease regularly. These results show that the active substance disappears in time in the AGL medium and turns into another product.

While it was 10.20 ng g<sup>-1</sup> at 0 min for Imidacloprid active substance, it was determined as 10.32 ng g<sup>-1</sup> at 240 min later. It was determined that there was no change between the first concentration and the last concentration depending on the time. These results show that the active substance is not affected by the AGL medium.

The time-dependent change in the AGL medium of 75 pesticide active ingredients spiked to the tomato sample is given in Table 4.

**Table 4.** Time-dependent change of spiked pesticide active substances in the AGL medium (ng g<sup>-1</sup>)

Active Substances (ng g <sup>-1</sup> )	0 (min.)	30 (min.)	60 (min.)	90 (min.)	120 (min.)	150 (min.)	180 (min.)	210 (min.)	240 (min.)	% Change
Spiroxamine	77.58	46.43	29.44	17.17	11.71	7.78	5.35	2.95	2.42	96.88
Diazinon	66.65	50.20	26.49	19.10	14.16	9.87	7.62	3.43	3.30	95.05
Thiodicarb	2.04	60.63	41.94	30.78	23.84	16.15	13.3	7.99	6.65	91.90
Chlorsulfuron	94.13	62.14	44.21	30.41	28.6	18.55	13.84	9.42	7.97	91.54
Thifensulfuronmethyl	69.79	51.02	42.12	29.64	26.39	21.27	16.24	10.14	10.38	85.12
Sethoxydim	84.01	57.92	34.29	26.56	22.55	24.86	21.23	14.37	14.64	82.57
Fenazaquin	85.82	74.87	48.92	36.90	38.54	31.61	25.48	16.97	15.39	82.07
Furathiocarb	85.40	75.66	47.60	35.29	38.89	39.69	29.15	19.51	17.11	79.97
Triasulfuron	76.60	62.50	50.18	41.45	34.87	29.37	24.64	16.58	17.13	77.64
Triallate	118.92	84.72	68.55	51.39	30.02	59.5	49.18	33.98	32.30	72.84
Aldicarb	99.51	87.80	66.33	58.52	53.47	38.92	38.38	33.00	30.93	68.92
Ethofumesate	76.63	90.10	60.02	55.66	49.94	37.89	32.55	28.01	26.14	65.89
Butocarboxim	108.37	102.4	72.29	69.05	58.02	48.03	46.93	40.26	39.99	63.10
Quizalofop-p-ethyl	114.67	107.20	71.44	54.63	44.56	72.12	57.9	43.21	42.89	62.60
Ethion	117.15	112.02	72.64	64.36	49.14	79.71	65.84	49.27	45.76	60.94
Tebufenpyrad	100.56	101.51	65.04	56.46	48.64	75.1	59.02	45.72	41.84	58.40
Methamidophos	65.52	60.80	52.34	46.34	41.21	37.56	34.44	29.54	27.36	58.24
Tecnazene	82.27	90.23	73.66	45.08	73.44	72.34	51.95	42.53	39.08	52.50
Quintozene	80.95	95.34	68.67	50.00	70.24	71.76	56.75	45.16	39.95	50.65
Dicofol	84.73	108.68	77.61	54.78	71.25	68.56	59.19	50.11	44.61	47.35
Fonofos	62.72	71.38	52.00	41.27	47.95	58.65	42.76	33.75	34.43	45.11
β-endosulfan	81.65	107.22	66.77	60.73	70.69	63.06	61.31	59.07	45.46	44.32
Hexachlorobenzene	71.95	86.42	64.43	51.52	70.37	65.35	54.11	44.69	40.37	43.89
Pyridate	59.77	38.62	33.56	45.99	44.54	54.15	46.63	38.4	34.70	41.94
Chlorpyrifos	82.31	105.15	72.94	61.02	78.72	75.59	65.47	56.08	47.99	41.70
Quinalphos	91.24	96.68	76.67	61.05	63.49	78.67	61.99	52.29	53.49	41.37
α-endosulfan	78.07	102.30	67.12	57.73	72.81	68.07	61.00	54.71	45.91	41.19
Clodinafop-propargyl ester	92.6	102.00	82.17	62.32	73.32	86.72	63.48	55.75	55.95	39.58
Tebufenozide	109.72	123.48	103.32	80.51	88.93	95.00	77.76	74.36	70.63	35.62
Fludioxonil	88.43	106.37	91.24	62.08	96.34	93.61	71.75	68.74	58.87	33.43
Difenoconazole	84.53	87.94	57.48	61.20	74.52	75.39	66.80	55.42	56.35	33.34
Triazophos	100.1	100.50	91.05	77.94	91.89	87.36	72.75	72.10	68.20	31.87
Etofenprox	104.81	47.93	45.41	86.37	75.72	95.46	91.56	75.27	72.00	31.31
Carboxin	102.18	102.29	74.92	64.29	69.91	65.94	68.24	67.18	70.43	31.07
2,4-DDD	80.27	108.38	71.07	76.35	84.07	75.13	80.04	73.68	58.04	27.69
4,4-DDD	79.26	106.73	69.61	74.87	82.34	74.79	79.46	72.06	57.37	27.62
2,4-DDT	73.77	107.30	65.03	69.53	75.95	65.09	73.78	67.43	54.12	26.64
Boscalid	77.86	82.72	74.74	66.97	71.98	79.44	66.73	64.48	62.94	19.15
Penconazole	83.47	88.82	72.42	74.84	72.02	78.42	72.35	69.13	72.93	12.64
Malathion	86.12	85.28	80.46	77.16	77.96	76.07	75.19	74.93	75.67	12.13
Hexaconazole	75.86	78.03	63.69	69.67	64.49	69.86	68.34	62.28	68.24	10.05
Triticonazole	85.15	89.16	70.87	81.12	82.91	81.81	78.27	78.77	77.06	9.51
Myclobutanil	69.89	72.90	63.38	63.59	65.39	69.96	65.71	64.48	63.40	9.28
Tetraconazole	81.77	86.04	74.33	71.54	76.45	80.97	77.71	75.26	74.20	9.26
Molinate	77.69	76.91	72.19	71.05	73.18	69.12	64.82	68.73	71.12	8.46
Methiocarb	82.74	86.49	83.2	73.09	77.96	81.49	76.93	75.60	76.22	7.87
Propazine	95.29	97.95	89.64	90.98	87.14	89.59	88.00	86.02	89.58	5.99
Azoxystrobin	88.16	88.37	86.71	83.77	83.54	83.28	82.95	84.07	83.26	5.56
Atrazine	90.61	95.02	87.55	90.21	85.07	84.21	86.69	84.27	85.73	5.39
Triadimenol	92.36	95.84	80.55	88.88	87.65	86.09	82.52	84.62	87.46	5.30
Tributylazine	85.5	86.98	78.99	82.92	78.04	79.52	77.61	76.06	81.55	4.63
Benalaxyl	76.64	104.76	71.58	73.64	77.13	64.91	73.31	82.77	74.38	2.95
Ethoprophos	74.74	84.98	3.62	71.12	78.44	72.88	65.31	72.17	73.09	2.21
Parathion ethyl	50.71	77.65	66.6	29.12	60.22	56.87	57.35	40.83	49.61	2.17
Alachlor	89.56	87.92	80.13	91.06	85.48	87.38	82.52	82.73	88.14	1.59
Esfenvalerate	37.97	50.90	45.25	43.39	46.95	38.42	44.43	44.64	37.38	1.55
Fenvalerate	59.93	89.68	65.31	64.65	67.31	50.62	65.11	78.90	59.16	1.28
Diphenamid	87.59	87.89	82.89	83.62	81.78	86.86	80.32	86.82	86.62	1.11
Metolachlor	44.23	48.33	42.33	43.83	43.98	44.01	42.75	41.92	44.16	0.16
Prochloraz	91.69	97.12	71.62	88.03	79.80	86.15	86.86	80.78	91.55	0.16
Lenacil	56.37	57.03	55.38	55.38	52.47	55.90	51.45	54.77	56.59	-0.41
Diethofencarb	82.33	88.19	80.21	75.38	80.30	82.74	77.42	78.58	82.77	-0.54
Monolinuron	84.71	83.37	80.71	77.82	78.83	79.64	77.98	82.50	85.47	-0.90
Bupirimate	79.93	84.55	75.54	80.29	74.32	76.57	76.88	79.22	80.69	-0.96
Acetamiprid	94.43	104.34	86.07	92.76	86.01	79.59	84.94	91.01	95.63	-1.27
Heptanaphos	64.5	64.11	63.84	64.89	60.98	62.86	63.79	64.88	65.53	-1.59
Imazalil	81.77	85.04	79.86	86.14	82.43	81.69	83.03	83.11	83.08	-1.60
Dimethoate	97.52	101.19	88.78	94.61	89.73	84.01	89.26	92.87	99.10	-1.63
Omethoate	89.72	94.88	81.02	90.51	90.20	77.11	85.82	77.57	91.23	-1.68
Cymoxanil	93.38	101.74	79.94	88.40	81.42	75.66	84.26	87.43	95.02	-1.76
Prometryn	91.91	93.38	88.65	95.67	89.31	90.10	90.81	96.81	94.68	-3.02
Metalaxyl-M	78.4	76.18	78.09	79.01	76.26	74.20	78.37	85.84	81.40	-3.83
Trichlorfon	84.93	90.82	79.56	85.51	83.22	76.75	82.27	83.81	88.28	-3.94
Paraoxon ethyl	92.37	95.54	92.59	94.70	89.91	89.12	88.20	93.00	96.50	-4.48
Acephate	68.00	69.75	73.97	70.86	69.87	72.47	71.75	70.22	71.07	-4.52

When evaluated according to the above results and chemical properties of 75 pesticides active substance in the AGL medium, for active substances (1-10 units) with a change rate of over 70% (96.88-72.84%), it was determined that there was a statistically decrease in their concentration in time intervals between 0-240 min. When we look at the active substances (11-30 units) which show a change rate below 70% (68.92-12.13%); it was observed that there was no statistical decrease time-dependent, but there was a certain thought at different rates between the initial concentration and the final concentration after 240 min. According to the results in the table, 20 (41-60 units) active substance was determined to be almost little of time-dependent change (10.05-0.16%) between the first and the last concentrations. It was determined that AGL does not affect these active substances. A negative shot (-0,41-4,52) according to 0 min compared 240 min concentrations of 15 (61-75 units) active substances was observed. The AGL was determined to have a positive effect on these active substances.

**Table 5.** pKa values of pesticide active substances

Active Substances	Chemical Class	pKa
Diazinon	Organophosphorus	2.60
Chlorsulfuron	Sulfonylurea	3.40
Thifensulfuronmethyl	Triazinylsulfonylurea	4.00
Sethoxydim	Cyclohexanedionedioxime	4.40
Triasulfuron	Triazinylsulfonylurea	4.64
Penconazole	Triazole	1.51
Tetraconazole	Triazole	0.80
Propazine	Triazine	1.70
Atrazine	Triazine	1.60
Terbuthylazine	Triazine	2.00
Prochloraz	Midazole	3.80
Lenacil	Uracil	10.70
Bupirimate	Pyrimidinol	5.00
Acetamiprid	Eonicotinoid	0.70
Imazalil	Imidazole	6.49
Cymoxanil	-	9.70
Prometryn	Triazine	4.10
Acephate	Organophosphorus	8.35

It was observed that organophosphorus pesticides reacted differently from the high rate of change to a low rate of change in the time-dependent AGL medium. Although active substances are in the same chemical class and behave differently; they were determined that the pKa values of the active substances differ solubilities in water, the type and number of atoms it contains, of the molecular formula, of the bond structure between atoms, whether it contains a ring structure.

In the AGL medium of carbamate pesticide groups generally highly was dissolved and turned into other products and was determined that carbamate pesticides bound to N-phenyl and N-methyl were not affected by the AGL medium.

Organochlorinated pesticides were determined to vary between 50-25% in the AGL medium. It was determined that pesticides with Trizalo and Triazine groups were generally not affected by the AGL medium. When looking at other groups (Imidazole, Uracil, Pyrethroid, Strobilurin) pesticides, the change rates chemical structure, water-solubility, pKa values, bond structure, etc., it was observed that it changed depending on the reasons.

Zawiyah et al. in a study did in (2007); they had been examined Organochlorine and Pyrethroid group pesticide residues in fruit and vegetable samples collected from the markets in Malaysia. It determined the active substance of Cypermethrin as an average of 0.47 mg kg<sup>-1</sup> in 38 of 302 vegetable

samples. They stated that the active substance found was between 0.16-1.48 mg kg<sup>-1</sup> in tomato, paprika, bean, bell pepper, and local products (Zawiyah et al., 2007).

When evaluated according to pKa values, it was determined that the active substances with small pKa values dissolved more and turned into another structure, and the active substances with large pKa values were not affected by the medium.

According to the above all evaluations, it was determined that the active substances in different classes behave differently, carbamate pesticides dissolve better in the AGL medium, organochlorinated pesticides dissolve less than according to carbamate pesticides, organophosphorus pesticides give react differently, and the triazolo and triazine group pesticides are not affected by the medium. In general, the effect of AGL on pesticides was determined that the chemical structure of the active substance, its water solubility, pKa values, open formula structure, whether it was the ring structure and, have changed as time-dependent.

## CONCLUSION

In the study carried out in AGL medium, in the analysis made for a total of 240 min every half hour of tomato sample containing pesticide active substance was observed that the active substance of Trifloxystrobin changed against time. The change in Imidacloprid active substance could not be observed. It was determined that the effect of the AGL is different for each active substance. According to the results of the study carried out with 75 active substances spiked to the tomato sample in the AGL medium; depending on time, change in the concentration of a large part of active substances was observed. It was determined that the concentrations of some pesticide active substance were not affected at all. The water solubility, polarity, pKa values, closed and open formulas of the pesticide class were determined to be effective in this medium. It is thought that detailed studies should be done about what the active substances turn into.

## Conflict of Interest

The article authors declare that there is no conflict of interest between them.

## Author's Contributions

The authors declare that they have contributed equally to the article.

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