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Degradation of the Selected Pesticides by Gas Discharge Plasma

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┤ **Abstract** ├

As increasing the use of pesticides both in number and amount to boost crop production, consumer concerns over food quality and safety with respect to residual pesticides are also continuously increasing. However, there is still lacking of information that can effectively help to remove residual pesticides in foods. In recent years, contaminant removal by gas (or) glow discharge plasma (GDP) attracts great interests on environmental scientists because of its high removal efficiency and environmental compatibility. It was shown to be effective for the removal of some organophosphorus pesticides, phenols, benzoic acid, dyes, and nitrobenzene on solid substrate or in aqueous solution. This work mainly focuses on the removal of wide range of residual pesticides from fresh fruits and vegetables. As for preliminary study, the experiments were carried out to investigate whether GDP can be used as an effective tool for degrading target pesticides or not. With this objective, 60 selected pesticides drop wised onto glass slides were exposed to two types of GDP, dielectric barrier discharge plasma (DBDP) and low pressure discharge plasma (LPDP), for 5 min. Then, they were washed with 2 mL MeCN which were collected and used for determination of remaining concentration of pesticides using LC-MS/MS. Among selected pesticides, degradation of 18 pesticides (endosulfan-total was counted as one pesticide) by GDP could not be examined because control treatments, which were left in ambient environment, of those pesticides recovered less than 70% or even did not recover. However, majority of tested pesticides (42) were degraded by both types of GDP with satisfactory recovery (>80%) of control sample. Pesticides degradation ranged from 66.88% to 100% were achieved by both types of plasma except clothianidin which degradation in LPDP was 26.9%. The results clearly indicate that both types of gas discharge plasma are promising tools for degrading wide range of pesticides on glass substrate.

Key words Gas discharge plasma, dielectric barrier discharge plasma, low pressure discharge plasma, pesticides, food safety

Introduction

Pesticides are widely used in producing food and feed. The role of pesticides in modern agriculture is continuously increasing and their contribution to crop protection is also continuously increasing. Pesticides residue may remain in small amount in or on agricultural products and processed foods. As a result, consumers are becoming aware of food quality and safety issues, and are realizing the need to be selective about the foods. Therefore, governments take legislative action to ensure that only safe food of acceptable quality is sold, and that the risk of food-borne health hazards is minimized. To ensure the safety of foods, most governments regulate the maximum level of

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Table 1. Selected pesticides to be treated with GDP

No.	Pesticides Name	Group	Type
1	Acetamiprid	Neonicotinoid	Insecticide
2	Aldicarb	Carbamate	Insecticide, acaricide, nematicide
3	Azoxystrobin	Methoxyacrylate	Fungicide
4	Boscalid	Carboxamide	Fungicide
5	Carbaryl	Carbamate	Insecticide, acaricide
6	Carbendazim	Benzimidazole	Fungicide
7	Carbofuran	Carbamate	Insecticide, nematicide
8	Chlorantraniliprole	-	-
9	Chlorfluazuron	Benzoylurea	Insecticide
10	Chlorothalonil	Chloronitrile	Fungicide
11	Chlorpyrifos	Organophosphate	Insecticide
12	Chlorpyrifos	Organophosphate	Insecticide
13	Clothianidin	nitromethylene; neonicotinoid	Insecticide
14	Diazinon	Organophosphate	Insecticide, acaricide
15	Diethofencarb	N-phenyl carbamate	Fungicide
16	Difenoconazole	Triazole	Fungicide
17	Diflubenzuron	Benzoylurea	Insecticide
18	Dimethomorph	Cinnamic acid	Fungicide
19	Dinotefuran	nitromethylene; neonicotinoid	Insecticide
20	Endosulfan (Total)	Organochloride	Insecticide, acaricide
21	EPN	Organophosphate	Insecticide, acaricide
22	Fenbuconazole	Triazole	Fungicide
23	Fenobucarb	Carbamate	Insecticide
24	Fenothiocarb	Carbamate	Acaricide
25	Fenpropathrin	pyrethroid	Acaricide, insecticide
26	Fenthion	Organophosphate	Insecticide
27	Fludioxonil	Phenylpyrrole	Fungicide
28	Flufenoxuron	Benzoylurea	Insecticide, acaricide
29	Fluquinconazole	Triazole	Fungicide
30	Hexaconazole	Triazole	Fungicide
31	Imibenconazole	Triazole	Fungicide
32	Imidacloprid	Neonicotinoid	Insecticide
33	Indoxacarb	Oxadiazine	Insecticide
34	Iprobenfos	Phosphorothiolate	Fungicide
35	Iprodione	Dicarboximide	Fungicide
36	Isoprothiolane	Phosphorothiolate	Fungicide, plant growth regulator
37	Kresoxim-methyl	Oximinoacetate	Fungicide
38	Lufenuron	Benzoylurea	Insecticide, acaricide
39	Metconazole	Triazole	Fungicide
40	Methidathion	Organophosphorus	Insecticide, acaricide
41	Methomyl	Carbamate	Insecticide, acaricide
42	Methoxyfenozide	Diacylhydrazine	Insecticide
43	Myclobutanil	Triazole	Fungicide
44	Pendimethalin	Aniline	Herbicide
45	Phenthoate	Organophosphorus	Insecticide, acaricide
46	Prochloraz	Imidazole	Fungicide
47	Prometryn	Trizine	Herbicide
48	Pyraclostrobin	Strobilurin	Fungicide
49	Pyridaben	-	Insecticide, acaricide
50	Pyrimethanil	Anilinopyrimidine	Fungicide
51	Simazine	Trizine	Herbicide
52	Tebuconazole	Triazole	Fungicide
53	Tebufenozide	Diacylhydrazine	Insecticide
54	Tebufenpyrad	Pyrazole	Acaricide
55	Tetraconazole	Triazole	Fungicide
56	Thiacloprid	Neonicotinoid	Insecticide
57	Thiamethoxam	Neonicotinoid	Insecticide
58	Tolclofos-m	Organophosphate	Fungicide
59	Tricyclazole	Reductase	Fungicide
60	Trifloxystrobin	Oximinoacetate	Fungicide

each permitted pesticide residue (MRLs).

However, pesticide residues are still observed in Korea (Min *et al.*, 2011). Consumers' concerns are therefore still increasing regarding food safety issues. For this reason, removal of pesticides residue from market foods becomes a paramount important with respect to food safety.

On the other hand, recently emerging technologies (eg., advanced oxidation processes-AOPs, zerovalent iron-ZVI) for the removal of pesticides residue are mainly focusing onto residue from soil and water (Min *et al.*, 2009 and 2011; Glass, 1972; Hofstetter *et al.*, 2003; Ghauch and Suptil 2000; Satapanajaru *et al.*, 2003), and are obviously unsuitable to apply for fresh fruits and vegetables due to the necessity to add external elements into reaction media. The main disadvantage of these techniques for the use in food is the need to add external reagents, which are hazardous to human, into the reaction medium. Moreover, chemical oxidation also often results in incomplete destruction of pesticides molecules and tends to the formation of undesirable by-products (Ikehata and El-Din, 2005). Among the methods developed so far, ozonation may be the best way for the removal of residual pesticides from fruits and vegetables since it has a long history of investigation for aqueous pesticide degradation (Reynolds *et al.*, 1989; Rice, 1997). However, its removal efficiency to certain pesticides is relatively low compare to other AOPs such as O_3/H_2O_2 (Ikehata and El-Din, 2005). There is still lacking of information about removal of residual pesticides from fresh fruits and vegetables.

In recent years, contaminants removal by gas discharge plasma (GDP) attracts great interests of environmental scientists because of its high removal efficiency and environmental compatibility. Plasma is more or less ionized gas. It consists of electrons, ions and neutrals which are in fundamental and excited states. The feature of GDP is that high energy electrons generated from plasma provide sufficient energy to dissociate the molecules of the feed gas or target contaminants producing various active species such as H_2O_2 and $^\bullet OH$ (Hickling, 1971; Susanta *et al.*, 1998). Recent studies have shown that phenols, benzoic acid, aniline, dyes, and nitrobenzene could be effectively degraded by GDP (Liu and Jiang, 2005; Gao

et al., 2003; Tezuka M. and Iwasaki M., 1999 and 2001; Hu *et al.*, 2001; Gao *et al.*, 2003; Wang *et al.*, 2007). Degradation of organophosphorus pesticides, parathion, dichlorvos, and omethoate on solid substrate by GDP was also reported (Bai *et al.*, 2010; Bai *et al.*, 2009; Kim *et al.*, 2007). It is interesting that GDP can provide reductive reaction as reported by Wang and Jiang, 2008. In their experiment, Cr (Ⅵ) in aqueous solution was reduced to Cr (Ⅲ) after exposed to GDP for 15 min.

However, to the best of our knowledge, no report reveals the degradation of other pesticides by GDP rather than organophosphates as described above. This field of science is still a gap to be explored not only for the issues of food safety but also for the scientific significances. Since contaminant degradation by GDP is achieved by reactive species in the gaseous phase, this will be safer technology for the removal of residual pesticides from fresh fruits and vegetables. This work will be the first attempt to observe the effectiveness of GDP for degrading wide range of pesticides in agricultural commodities. Moreover, this work will help fulfill the demands of consumers for safe food with acceptable quality.

As for preliminary study, the experiment was conducted to investigate whether GDP can be used as an effective tool for degrading wide range of pesticides or not without using real fruits and vegetables. To this point, target pesticides were selected based on diversity in chemical structures and properties, their wide use in Korea, and potential hazardous effect on human being. List of selected pesticides are shown in Table 1.

Materials and Methods

Chemicals

Pesticides were purchased from Dr Ehrenstorfer (GmbH), Augsburg, Germany. Solvent acetone and acetonitrile were purchased from Merck (KGaA), Darmstadt, Germany.

LC−MS/MS condition

Precursor ions and product ions were predetermined at scan mode. The fragmentor voltage and collision energy

Table 2. LC-MS/MS set up condition for selected pesticides

No.	Compound Name	Precursor Ion	Frag-mentor	Product Ion (Q1)	C E (Q1)	Product Ion (Q2)	C E (Q2)	Ret Time (min)
1	Acetamiprid	223.07	80	126.01	15	56	15	8.702
2	Aldicarb	213	90	116	10	89.1	10	9.595
3	Azoxystrobin	404.12	120	372.1	10	344.1	15	12.203
4	Boscalid	343	160	307.1	12	271	28	12.625
5	Carbaryl	202.1	54	145.1	3	127.1	30	10.74
6	Carbendazim	192.2	98	160.1	15	105.1	42	7.635
7	Carbofuran	222.2	85	165.1	5	123.1	20	10.503
8	Chlorantraniliprole	482	110	450.9	13	283.9	9	8.362
9	Chlorfluazuron	540	120	382.9	20	157.9	15	18.738
10	Chlorpyrifos	350	88	198	18	97	33	15.575
11	Chlorpyrifos	350	88	198	18	97	33	15.694
12	Clothianidin	250	86	169.1	8	132	12	6.145
13	Diazinon	305.1	125	169.1	19	153.1	21	14.405
14	Diethofencarb	268.1	65	226.1	5	152	20	9.43
15	Difenoconazole	406.1	144	250.9	25	75	108	12.464
16	Diflubenzuron	310.8	92	157.8	10	140.8	32	10.267
17	Dimethomorph	388.1	135	301.1	20	165	35	8.566
18	Dinotefuran	203.1	80	157.1	3	129.1	6	5.658
19	EPN	324.1	113	296.1	7	157	20	14.278
20	Fenbuconazole	337.2	133	125	37	70.1	22	12.553
21	Fenobucarb	208.1	80	152	5	95.1	10	9.261
22	Fenothiocarb	254.1	85	72.1	12	160.1	4	13.352
23	Fenpropathrin	350.2	110	125	15	97.1	35	20.118
24	Fenthion	278.9	80	246.8	9	168.9	16	13.748
25	Fludioxonil	265.8	60	228.8	7	184.8	24	12.019
26	Flufenoxuron	489	138	158	16	141	48	17.619
27	Fluquinconazole	375.7	140	348.7	18	306.8	25	9.994
28	Hexaconazole	314.1	120	159	31	70.1	18	10.953
29	Imibenconazole	411	100	171	15	125	20	14.409
30	Imidacloprid	256.06	80	209.06	10	175.03	10	8.512
31	Indoxacarb	528.1	110	202.9	41	149.9	21	14.091
32	Iprobenfos	289.1	75	205	3	91	25	10.95
33	Iprodione	329.8	90	244.8	8	173.8	28	13.034
34	Isoprothiolane	291	80	231	5	189	18	11.181
35	Kresoxim-m	314.1	83	222.1	8	116.1	33	12.388
36	Lufenuron	511	125	157.9	15	140.8	40	16.686
37	Metconazole	320.2	114	125	44	70.1	27	13.095
38	Methidathion	303	59	145.1	1	85.1	15	9.269
39	Methomyl	163.1	45	106.1	4	88.1	3	5.953
40	Methoxyfenozide	313	100	149	5	91	25	10.127
41	Myclobutanil	289.2	110	125.1	38	70.1	15	12.356
42	Pendimethalin	282.2	133	212	4	194.3	16	15.648
43	Phenthoate	321.1	85	107.1	25	79.1	45	13.013
44	Prochloraz	376.1	93	308	5	70.1	23	11.402
45	Prometrin	242.3	135	200.1	15	158.1	25	12.833
46	Pyraclostrobin	388.1	120	194.1	10	163	15	13.393
47	Pyridaben	365.2	96	309.1	7	147.1	22	20.881
48	Pyrimethanil	200.1	120	183	25	107.1	25	9.72
49	Simazine	202.1	125	124.1	15	104	25	10.106
50	Tebuconazole	308.2	125	125.1	45	70.1	23	10.235
51	Tebufenozide	353.2	90	297.2	5	133.1	15	11.53
52	Tebufenpyrad	334.2	150	145.1	25	117.1	40	16.857
53	Tetraconazole	372.1	124	159	40	70.1	23	12.291
54	Thiacloprid	253	90	186	10	126	20	6.572
55	Thiamethoxam	292.03	80	211.04	10	181.03	20	7.746
56	Tolclofos-m	301.1	110	125	17	269	12	14.307
57	Tricyclazole	190.2	130	136.2	30	163.2	22	8.67
58	Trifloxystrobin	409.1	120	206.1	10	186.1	15	15.723

that gave the most intense peak of selected ions of respective pesticide were used as analytical condition of LC-MS/MS. Dynamic multi-reaction monitoring mode was used for quantitative analysis at positive ionization. Detail LC-MS/MS conditions for selected pesticides were shown in Table 2.

GC-ECD condition

Agilent 6890-N GC coupled with electron capture detector was used for analysis of chlorothalonil and endosulfan (total). Restek-931000 (30 m × 320 μm × 0.50 μm i.d) column was mounted in the oven where temperature programmed from 100℃ (hold 3 min) to 280℃ (hold 15 min) at the rate of 15℃ min^{-1}. Injection port and detector temperature were set at 280℃ and 310℃ respectively. Post running time was 10 min at 280℃. N_2 was used as carrier gas with flow rate of 1 mLmin^{-1}. Sample injection was conducted at splitless mode with injection volume of 2 μL.

GDP types and condition

Two types of plasma, dielectric barrier discharge plasma (DBDP) (PL-2011, Plasmalife Co., Incheon, Korea) and low pressure discharge plasma (LPDP) (Cute-B, Femto Science Inc., Hwaseong, Korea) were used in this experiment. In DBDP, two electrodes were covered by dielectric barriers and glow discharge was created between them when potential differences were provided using 50 kV d. c. discharge voltage at pulse mode with the frequency of 50 kHz. It was operated at atmospheric pressure using 2.65 mm discharge length and 1.25 Amp current. In LPDP, dielectric cylinder is surrounded by magnetic coil. 1.5 kV d. c. discharge voltage at pulse mode with the frequency of 20 kHz from antenna propagated along plasma tube. Once plasma was created, it flowed from source chamber to process chamber where the substrate was placed. LPDP was operated at the pressure of 3-0.5 torr using 45 mm discharge length and 0.35 Amp current. Oxygen was used as feed gas in both types of plasma.

Experimental Procedure

Effect of GDP type on pesticide degradation

Standard stock solutions of 1000 ppm were made in both acetone and acetonitrile for each pesticide. Working standard solutions were made by diluting stock solution with respective solvent. Two replicate samples of each pesticide for each type of plasma were prepared. A 10 μL of 10 ppm standard in acetone was drop wised onto glass slide and left until complete solvent evaporation was achieved. The glass slides were then exposed to DBDP and LPDP. After 5 min of plasma treatment, samples were washed with 2 mL acetonitrile and filtered through 0.2 μm PTFE filter. Then, they were kept in the deep freezer at -20℃ until use for analysis in LC-MS/MS. Control samples were prepared using the same method and washed after 5 min leaving at ambient condition. The amount of solvent acetonitrile needed for washing pesticides from glass slide was predetermined before actual experiment was started. It was found that all pesticides' recovery were greater than 80% by washing with 2 mL of acetonitrile just after solvent evaporation on glass slide.

Effect of treatment time on degradation of selected pesticides

Pesticides, carbendazim, fludioxonil, imidacloprid, myclobutanil, thiamethoxam, and tricyclazole, are selected to study the effect of plasma treatment time on their degradation rate and amount. A 10 μL of 10 ppm standards was drop wised onto glass slides. After complete evaporation of solvent, samples were exposed to both DBDP and LPDP for 30s, 1, 3, and 5 min. Determination of residual pesticide concentration was conducted in LC-MS/MS as described above. Concentration of residual pesticides was plot against treatment time. To calculate degradation kinetics and half-lifes, $ln[C_t/C_0]$ vs time was plot for 1st order kinetics and, $1/[C_t]-1/[C_0]$ vs time for 2nd order kinetics. The slope of the linear regression line is the degradation rate constant (k) for respective pesticide. Half-life was calculated using $T_{1/2}$ = ln2/k for 1st order kinetics and $T_{1/2}$ = $1/k[C_0]$ for 2nd order kinetics. C_0, C_t, k, and $T_{1/2}$ stand

for initial concentration of pesticide, concentration at time (t), degradation rate constant, and half-life respectively.

Calculation of degraded pesticide

Pesticide concentration was calculated from detector response to treated samples using standard calibration curve in excel spread sheet. Lowest calibration point was set at limits of detection (LOD) of each pesticide. LOD was set at S/N of 5. Degradation of pesticide was calculated based-on recovery of control sample that was used as initial concentration of pesticide in the following equation:

Degradation (%) = $(1 - C_t/C_0) \times 100$.

Where, C_t = concentration of pesticide at time (t)

$\quad\quad C_0$ = initial concentration of pesticide

Results and Discussion

Effect of plasma type on pesticide degradation

Control sample of some of target pesticides listed in Table 1, including organophosphorous pesticides, did not recover after 5 min leaving on glass slide at ambient condition. Therefore, their degradation by GDP couldn't be observed as shown in Table 3.

However, majority of target pesticides (42) showed promising degradation efficiency of GDP giving satisfactory recovery of control sample (> 80%) as can be seen in Table 4. It was found that degradation of most pesticides ranged from 66.88 to 100%. However, degradation of pesticide clothianidin by LPDP was observed as 26.9% of initial concentration. Pesticide degradation by DBDP is likely to be greater than that by LPDP in many cases. Therefore, data were input into Sigma-Plot 10.0, Systat Software, Inc. (San Jose, CA) for statistical analysis. Two-tailed student's t-test was carried out to compare the results. Calculated t-values of some pesticides such as azoxystrobin, boscalid, carbendazim, fludioxonil, imidacloprid, thiamethoxam, and tricyclazole are greater than tabulated t-value 4.30 for 2 degree of freedom (p = 0.05).Therefore the degradation of those pesticides by DBDP is significantly greater than the degradation of those pesticides by LPDP

Table 3. List of pesticides which control recovery is lower than 70% so that the degradation induced by GDP can't be proceeded

No	Pesticides Name	Recovery (%)			Degradation (%)		LOD (ppm)	R²
		Control	DBDP	LPDP	DBDP	LPDP		
1	Acetamiprid	69.86±3.65	ND	15.09±1.96	100	78.4	0.005	1
2	Aldicarb	6.42±0.16	ND	ND	ND	ND	0.02	0.9999
3	Carbofuran	57.41±2.13	1.64±0.38	2.23±0.81	97.14	96.12	0.005	0.9999
4	Chlorothalonil	ND	ND	ND	ND	ND	0.05	0.9775
5	Chlorpyrifos	ND	ND	ND	ND	ND	0.0025	0.9999
6	Diazinon	ND	ND	ND	ND	ND	0.01	1
7	Endosulfan-Alpha	17.74±0.57	13.43±0.24	11.97±0.04	25.26	32.51	0.005	0.9999
8	Endosulfan-Beta	42.88±3.14	35.84±1.51	26.23±0.03	16.43	38.85	0.005	0.9988
9	Endosulfan-sulphate	74.67±2.51	48.39±2.99	29.50±0.15	35.19	60.49	0.005	0.9952
10	Fenobucarb	ND	ND	ND	ND	ND	0.001	0.9999
11	Fenthion	ND	ND	ND	ND	ND	0.005	0.9996
12	Iprobenfos	67.09±11.15	0.03±0.004	0.46±0.52	99.95	99.32	0.005	0.9995
13	Iprodione	63.29±6.46	ND	24.46±9.67	100	61.36	0.01	0.9999
14	Methomyl	34.75±13.43	5.53±0.17	26.36±4.05	84.07	24.12	0.005	0.9992
15	Pendimethalin	ND	ND	ND	ND	ND	0.01	0.9986
16	Phenthoate	ND	ND	ND	ND	ND	0.0025	0.9998
17	Procymidone	15.64±9.89	ND	ND	-	-	0.005	1
18	Prometryn	60.56±1.10	1.84±0.10	1.94±0.003	96.96	96.79	0.005	0.9999
19	Pyrimethanil	ND	ND	ND	ND	ND	0.0025	0.9998
20	Tolclofos-methyl	ND	ND	ND	ND	ND	0.005	0.9994

at 95% confident level. However, some pesticides' degradation after 5 min of plasma treatment not differs in both types of plasma. This was observed in pesticides such as fenothiocarb, imibenconazole, difenoconazole, and myclobutanil. Such kind of degradation efficiency indicates that pesticide

degradation depends not only on type of plasma used but also on pesticide itself. Chemical structural differences of pesticide may play an important role in degradation process during plasma treatment.

Degradation of pesticides by GDP may be due to high

Table 4. List of pesticides which control recovery is greater than 80% and the calculated results of their degradation induced by GDP

No	Pesticides Name	Recovery (%)			Degradation (%)		LOD (ppm)	R^2
		Control	DBDP	LPDP	DBDP	LPDP		
1	Azoxystrobin	80.53±4.42	11.57±2.17	26.61±2.17	85.63	66.96	0.001	0.9998
2	Boscalid	83.53±4.30	12.78±4.44	33.51±5.32	84.69	59.88	0.005	0.9997
3	Carbaryl	81.73±2.05	ND	5.21±0.56	100.00	93.60	0.005	1
4	Carbendazim	89.05±5.99	10.91±3.22	29.49±1.96	87.75	66.88	0.001	1
5	Chlorantraniliprole	112.05±2.68	ND	ND	100.00	100.00	0.001	0.9913
6	Chlorfluazuron	113.45±3.35	ND	22.21±10.55	100.00	85.95	0.0025	0.9992
7	Clothianidin	82.52±2.81	13.01±8.9	60.32±6.33	84.24	26.91	0.005	0.9998
8	Diethofencarb	94.74±1.41	ND	ND	100.00	100.00	0.001	0.9996
9	Difenoconazole	95.95±4.14	ND	ND	100.00	100.00	0.0025	0.9996
10	Diflubenzuron	93.74±4.80	9.72±2.75	6.87±2.71	89.63	92.68	0.001	0.9988
11	Dimethomorph	95.45±3.09	6.50±3.01	13.88±2.28	93.19	85.46	0.001	0.9996
12	Dinotefuran	82.94±0.59	ND	20.99±3.52	100.00	74.69	0.005	0.9996
13	EPN	92.27±6.88	ND	ND	100.00	100.00	0.005	0.9999
14	Fenbuconazole	94.86±1.28	13.40±4.88	16.78±3.65	85.90	82.30	0.001	0.9994
15	Fenothiocarb	92.64±2.71	ND	ND	100.00	100.00	0.001	0.9996
16	Fenpropathrin	92.10±5.54	ND	ND	100.00	100.00	0.0025	0.9960
17	Fludioxonil	96.21±2.93	ND	17.05±3.15	100.00	82.28	0.01	0.9965
18	Flufenoxuron	92.11±1.46	6.34±0.79	5.91±1.91	93.11	93.58	0.001	0.9962
19	Fluquinconazole	83.54±2.03	8.46±0.50	8.50±0.44	89.87	89.82	0.001	0.9980
20	Hexaconazole	89.16±1.61	6.49±4.61	ND	92.72	100.00	0.001	0.9998
21	Imibenconazole	98.57 ± 3.44	ND	ND	100.00	100.00	0.005	0.9997
22	Imidacloprid	84.21±4.38	8.01±0.94	18.78±2.04	90.48	77.70	0.0025	1
23	Indoxacarb	79.39±2.48	7.99±3.06	13.41±0.20	89.94	83.11	0.0025	0.9988
24	Isoprothiolane	105.79±5.09	ND	ND	100.00	100.00	0.005	0.9993
25	Kresoxim-methyl	97.47±0.82	ND	ND	100.00	100.00	0.0025	0.9998
26	Lufenuron	133.79±13.38	6.48±1.49	ND	95.15	100.00	0.001	0.9998
27	Metconazole	101.16±2.02	ND	12.45±1.59	100.00	87.70	0.005	0.9999
28	Methidathion	81.56±1.86	ND	ND	100.00	100.00	0.005	0.9996
29	Methoxyfenozide	96.69±2.54	9.99±4.28	4.81±0.64	89.67	95.02	0.001	0.9998
30	Myclobutanil	93.85±6.11	ND	ND	100.00	100.00	0.005	0.9998
31	Prochloraz	107.18±0.02	ND	ND	100.00	100.00	0.001	1
32	Pyraclostrobin	104.48±0.05	ND	6.05±1.88	100.00	94.20	0.001	0.9996
33	Pyridaben	111.95±0.08	ND	6.60±7.3	100.00	94.10	0.001	0.9999
34	Simazine	92.92±1.23	19.59±3.51	24.06±3.50	78.90	74.10	0.005	0.9999
35	Tebuconazole	96.38±1.57	ND	ND	100.00	100.00	0.005	0.9982
36	Tebufenozide	119.36±0.63	ND	4.28±1.02	100.00	96.41	0.001	0.9996
37	Tebufenpyrad	115.08±0.96	ND	ND	100.00	100.00	0.001	0.9999
38	Tetraconazole	95.56±7.85	8.24±0.58	12.19±3.11	91.40	87.20	0.001	1
39	Thiacloprid	105.85±0.27	8.64±5.54	16.09±2.30	91.84	84.80	0.001	0.9998
40	Thiamethoxam	90.74±0.42	5.19±2.20	29.54±2.30	94.28	67.44	0.001	1
41	Tricyclazole	83.87±0.99	ND	27.32±3.62	100.00	67.43	0.01	0.9998
42	Trifloxystrobin	98.18±1.57	5.47±0.66	3.63±0.26	94.43	96.30	0.001	0.9996

electron energy (up to 965 kJ/mol) generated in plasma. Comparing this electron energy with bond energy of some chemical bonding listed in elsewhere (Chang, 2002), it is obvious that plasma generated enough electron energy to dissociate most chemical bonds. On the other hand, it was reported that when potential difference was applied, electrons were accelerated and reach a sufficient energy to dissociate the molecules of feed gas leading production of active oxygen species such as $O_2^{-\bullet}$, $O^\bullet$ and $^\bullet OH$ where O_2 was used as feed gas. These oxidants are reportedly observed as the sources for the degradation of organo-phosphorous pesticides by O_2 plasma (Bai *et al.*, 2009).

Although exact degradation mechanism of target pesticides by GDP was not yet observed in this study, it is believed that pesticides degradation was achieved by one of the above mentioned processes.
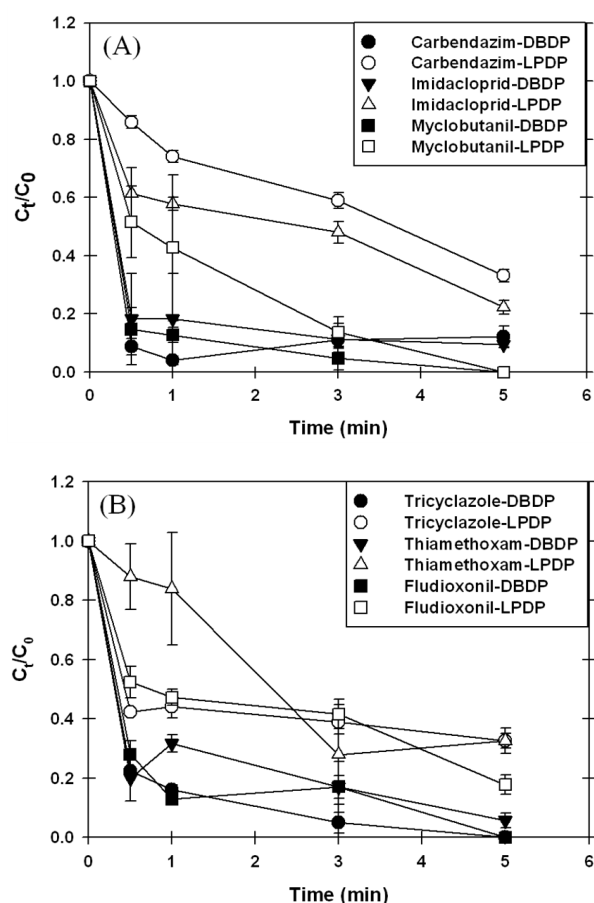
Fig. 1. Changes of pesticides' concentration with increasing treatment time by DBDP and LPDP (A) carbendazim, imidacloprid, and myclobutanil (B) tricyclazole, thiamethoxam, and fludioxonil. Error bars are standard deviation of mean.

Effect of treatment time on degradation of selected pesticides

6 pesticides were selected to explore the degradation behavior of pesticides when treated with GDP. Pesticides were selected based on the chemical structures and prop-erties to represent modern pesticides as much as possible. Moreover, the selection also base on the differences in degradation rate when subjected to GDP to better understand the degradation behavior. The changes in concentration of 6 selected pesticides with increasing treatment time were shown in Fig. 1, (A) and (B). The results indicate that degradation of all target pesticides significantly increased with treatment time (p = 0.01). DBDP showed excellent degradation efficiency in all cases. More than 80% degradation was achieved within 30s of treatment time while LPDP showed relatively slower degradation of pesticides. Trend of degradation of pesticides by DBDP are similar in all cases although it show different trend to LPDP and vise visa. This indicate that the degradation path way and mechanism could be different in two plasma types. Therefore, it is necessary to determine the degradation kinetics and parameters to clearly explain the degradation behavior of target pesticides by different plasma types.

The results of 1st and 2nd order kinetics along with regression coefficients and half-life values are reported in Table 5 and 6 respectively. As can be seen in Table 5 and 6, pesticides degradation by DBDP best fitted with 2nd order kinetics giving correlation coefficients of > 0.78 in all cases. In the case of carbendazim, myclobutanil, and tricyclazole, it was even greater than 0.95. This reveals that degradation of pesticides by DBDP involved more than one reactive species. Unlike DBDP, pesticides degradation by LPDP seemed to follow both 1st and 2nd order kinetics. Myclobutanil, tricyclazole, and fludioxonil which degradation was best fitted with 2nd order kinetics

Table 5. First order reaction kinetics and half-life

Pesticide	LPDP		
	k (min^{-1})	t$_{1/2}$(min)	R^2
Carbendazim	0.21	3.36	0.9712
Imidacloprid	0.26	2.67	0.8967
Thiamethoxam	0.25	2.76	0.7805

Table 6. Second order reaction kinetics and half-life

Pesticide	DBDP			LPDP		
	k ($mM^{-1}.min^{-1}$)	$t_{1/2}$(min)	R^2	k ($mM^{-1}.min^{-1}$)	$t_{1/2}$(min)	R^2
Carbendazim	80.19	0.05	0.9639	-	-	-
Imidacloprid	9.59	0.59	0.8606	-	-	-
Myclobutanil	42.90	0.16	0.9820	14.32	0.47	0.9835
Tricyclazole	26.04	0.15	0.9938	1.46	2.78	0.7372
Thiamethoxam	18.14	0.38	0.8511	-	-	-
Fludioxonil	15.20	0.43	0.7888	3.79	1.72	0.8906

whereas the rest of pesticides were best fitted with 1st order kinetics. These results clearly indicated that degradation of pesticides by DBDP and LPDP are achieved by different reaction path way and mechanism. Moreover, the degradation path way and mechanism depends not only on type of GDP used but also on pesticide itself as can be observed in myclobutanil degradation kinetic. Comparing calculated half-life values, it is found that pesticides degradation by DBDP is faster than that by LPDP.

Conclusion

According to the results of this experiment, it can be concluded that both types of GDP can be used as promising tools for the degradation of target pesticides. Degradation by DBDP is relatively faster than that by LPDP. Degradation behavior of pesticides differs from type of GDP used. In addition, the mechanism and pathway of degradation could depend not only on the types of GDP also on pesticides itself. Further study is still needed to observe detail mechanism of pesticide degradation by GDP, and degradation of pesticides in real fruit and vegetable samples.

Acknowledgement

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기체플라즈마에 의한 농약분해특성 연구

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요 약   식량증산을 위해 농약사용량이 증가함에 따라, 식품 중 잔류농약의 안전성 문제에 대한 관심은 날로 증가하고 있지만 효율적인 잔류농약 저감화 방법은 보급되지 못하고 있는 것이 현실이다. 최근에 기체 플라즈마에 의한 오염물질 제거는 고효율성과 환경친화성으로 많은 주목을 받고 있다. 특히 플라즈마는 수질 및 고체 표면 중 유기인계살충제, 페놀, 벤조산, 염료, 니트로벤젠과 같은 오염물질의 제거에 큰 효과가 있는 것으로 알려지고 있다. 본 연구는 플라즈마를 이용하여 농식품 중에 잔류되는 농약의 제거 가능성을 알아보고자 대기압 및 감압플라즈마 플라즈마 발생 상태에서 60종의 농약을 대상으로 분해양상을 파악해보고자 시도하였다.시험용 농약을 유리판에 도포 후 대기압 및 감압 플라즈마 발생기에서 5분간 조사 후 잔류량을 확인 한 결과 대조구의 회수 분석결과가 70% 미만인 18종을 제외한 41종의 농약 분해율이 66.88-100%를 나타내었고, clothianidin은 감압플라즈마하에서 26.9%이 분해율을 보였다.

색인어   잔류농약, 분해, 감압플라즈마, 대기압플라즈마