

Dissipation Behavior of Organophosphorus Pesticides during the Cabbage Pickling Process: Residue Changes with Salt and Vinegar Content of Pickling Solution

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ABSTRACT: In this experiment, the behavior of 10 pesticides in three different cabbage pickling treatments has been studied. The brine used for pickling was made up with different salt and vinegar contents to determine the influence of different pickling solutions on pesticide dissipation and distribution. A modified QuEChERS and SPE method was established for the analysis of the pesticides in the cabbage and brine. It was found that different pesticides showed different dissipation patterns and finally represented dissimilar residue levels in the cabbage and brine. Statistical analysis was performed to compare the distinctions of these pesticides between each treatment and proved that salt content and pH value had certain influence on the dissipation and distribution of these pesticides during the pickling process. The data from this experiment would help to control pesticide residues in pickled cabbage and prevent potential risk to human health and environmental safety.

KEYWORDS: *organophosphorus pesticides, cabbage pickling, pesticide residue, food safety*

INTRODUCTION

Organophosphorus pesticides (OPPs), which lead to increased food production, are widely applied to control pests in agricultural practice throughout the world.¹ However, the heavy use of OPPs has caused problems of pesticide residues in food commodities, water, air, and soil.^{2–5} Worse, recently researchers have found most human acute toxicity incidents are linked with the intoxication of OPPs, especially OPP residues on vegetables and fruits.^{6,7} In this case, more and more attention has been paid to OPP residues and their metabolites on all kinds of food commodities. Nowadays, researchers study not only the dissipation of OPPs in the field but also the behavior of OPP residues during food production processes, such as cooking, storage, and home preparation. They found proper washing methods and high-temperature cooking could eliminate most of the OPP residues, whereas storage did not represent good removal efficiency.^{8–11} Nevertheless, there was little study on the residue behavior of OPPs during vegetable pickling processes.

Pickled vegetables are processed by preserving the fresh vegetable in a solution mixed with salt, vinegar, and other seasonings for a certain time. Vegetable pickling is a kind of fermentation process, which is mainly caused by lactic acid bacteria (LAB). In this process, some new compounds are produced by LAB, such as folacin and vitamin B12, which are also helpful to human health. Among all kinds of pickling vegetables, pickled cabbage is the most popular worldwide. In some Asian countries, especially Korea and Japan, pickled cabbage is eaten with most meals.^{12,13} Unfortunately, as the pesticides are used worldwide, the raw material cabbage is sometimes polluted to various degrees in different regions,^{3,14} which also causes problems in the pickled cabbage. On the other hand, the waste brine from the pickling process may also contain kinds of pesticides, which might do harm to the environment.^{15,16} Therefore, it is necessary to study the residue behavior of the pesticides during the cabbage pickling process.

In this experiment, we mainly studied the residue behavior of 10 OPPs (ethoprophos, dimethoate, sumithion, malathion, chlorpyrifos, isocarbophos, methidathion, tetrachlorvinphos, profenofos, and triazophos) during the cabbage pickling process. The 10 OPPs are widely used to control different insect pests in the soil and vegetables.¹ Among these OPPs, dimethoate, malathion, isocarbophos, tetrachlorvinphos, and triazophos are the most often applied in the cabbage cultivation process, which can eliminate aphids, caterpillars, Halcitidae, etc.^{17–20} Three kinds of brine, which were suitable for the growth of different LAB, were used for the pickling process. A simple method was established to determine the residues of the 10 OPPs in the pickled cabbage and brine. Furthermore, the dissipation and distribution of the 10 OPPs in the pickled cabbage and brine were studied, and the behaviors of the 10 OPPs were compared in the different pickling conditions. The obtained data and results will help us to better evaluate OPP residue levels in fresh cabbage used for pickling and also in the waste brine from the pickling process.

MATERIALS AND METHODS

Chemicals and Reagents. All pesticide standards (ethoprophos, dimethoate, sumithion, malathion, chlorpyrifos, isocarbophos, methidathion, tetrachlorvinphos, profenofos, and triazophos) were provided by the China Ministry of Agriculture Institute for Control of Agrochemicals. Triphenyl phosphate (99.8%) used as the internal standard was purchased from Aladdin (Shanghai, China). Stock standard solutions of all analytes were prepared in acetone at a concentration of 1 g/L and stored in the dark at 4 °C.

Acetonitrile, dichloromethane, Tween 80, and sodium chloride were of analytical grade and purchased from Sinopharm Chemical Reagent Beijing Co., Ltd. Acetone was of HPLC grade and obtained from

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Fisher Scientific (Fair Lawn, NJ, USA). Vinegar used in the experiment was purchased from a local supermarket. Primary–secondary amine (PSA) and graphitized carbon black (GCB) was supplied by Bonna-Agela Technologies.

Materials. Cabbages were purchased from the local market as the main material. To ensure the parallelism of the dissipation trials, cabbages selected for the experiment were from the same field and of similar size, weight, and maturity. All of the studied organophosphorus pesticides were not detected in the cabbages used for pickling.

Preparation of Spiked Cabbage. First, rotten and broken parts of the cabbages, which may affect the quality of the pickled cabbage, was discarded. One cabbage was evenly separated into four parts, and each part was considered to be the same. Each part of the cabbage was washed and cut into similarly sized pieces, and then 300 g of cabbage was weighed into a 1 L Redi-pak. Each Redi-pak was treated as a sampling point.

Then 1 mL of 1 g/L mixed pesticide standard solution was dissolved in 800 mL of water with 200 μ L of Tween 80. All of the 800 mL mixture was added into the 1 L Redi-pak to immerse the cabbage. After 1 h, the water solution was poured off and the spiked cabbage was washed with pure water three times to wipe off the OPP residues on the surface of the cabbage. Finally, the polluted cabbages were aired under room conditions.

Cabbage Pickling Process. To compare the dissipation behaviors of the OPPs under different pickling conditions, the cabbages were pickled in three different NaCl solutions: treatment A, 10% NaCl (m/m, aq); treatment B, 20% NaCl (m/m, aq); and treatment C, 10% NaCl with 0.6% vinegar (m/m, aq). In this way, we compared the dissipation behavior of the OPPs under different pickling conditions. Eight hundred milliliters of the NaCl solution was added into the Redi-pak and then the Redi-pak was covered with a frosted glass cap. All samples were stored at 25 °C in the dark.

The controlled experiment was conducted with free cabbages, whereas other operations were the same as mentioned above.

Sampling. Three replicates were sampled from each treatment at different time intervals (0 h and 1, 3, 5, 7, 14, 21, 28, and 35 days). Both the pickled cabbage and the waste brine from pickling were collected for analysis. The pickled cabbage was washed three times with tap water before being homogenized by a blender. The brine from pickling was passed through a filter paper by gravity, and the filtrate was collected for analysis. All of the samples were stored at –20 °C before the extraction procedure.

Sample Preparation of Pickled Cabbage. Ten grams cabbage sample was exactly weighed into a 50 mL polypropylene centrifuge tube, and 20 mL of acetonitrile was added as the extraction solvent. The tube was stirred for 3 min on a vortex mixer, and then 2 g of NaCl was added to help separate the acetonitrile from the water. Finally, the mixture was centrifuged at 2425g for 3 min, and the acetonitrile solution was transferred into a pear-shaped flask. The extraction procedure was repeated with another 20 mL of acetonitrile. Most of the acetonitrile was removed by vacuum evaporation at 35 °C to about 1 mL and then dried with a stream of nitrogen. The extracts were dissolved in 1.0 mL of acetone and transferred into a 2 mL plastic tube containing 200 mg of PSA and 5 mg of GCB. The plastic tube was stirred for 30 s on a vortex mixer and then centrifuged at 2000g for 30 s. Finally, the purified acetone solution was combined with a triphenyl phosphate solution (0.4 mg/L, in acetone) at the rate of 1:1, and the mixture was stored at 4 °C for further GC analysis.

Sample Preparation of Brine from Cabbage Pickling Process. A simple SPE method was developed to clean up the brine sample. The SPE column (Thermo Fisher, Hypersep-C18, 500 mg, 6 mL) was preconditioned by 5 mL of methanol and then equilibrated with 10 mL of tap water. Then 50.0 g of brine sample was loaded into the SPE column under a certain negative pressure. When the SPE column was completely dry, 10 mL of dichloromethane was added as the eluent. All 10 mL of dichloromethane was collected in a cuvette and then dried under a stream of nitrogen at 35 °C. One milliliter of acetone was used to dissolve the extracts and also mixed with a triphenyl phosphate solution (0.4 mg/L, in acetone) at the rate of 1:1 for GC analysis.

GC-FPD Analysis. The procedure of separation, identification, and quantification was performed on an Agilent 6890N gas chromatograph with a flame photometric detector (GC-FPD) system and a 10 μ L autosampler. One microliter of the prepared sample was injected and separated on the HP-5 (5% phenyl, 95% methylpolysiloxane, 30 m \times 0.25 mm i.d. \times 0.25 μ m) capillary column, which was provided by J&W Scientific (Folsom, CA, USA). The injection port was set in the splitless mode at 270 °C with a splitless time of 0.47 min. The FPD detector was at a temperature of 250 °C and fed with 100 mL/min of purified compressed air, 75 mL/min of hydrogen (>99.999%), and 25 mL/min of nitrogen (>99.999%) as auxiliary gas. Nitrogen was also used as the carrier gas at a flow rate of 1.0 mL/min. The temperature program of the oven was started at 100 °C, increased to 220 °C at a rate of 20 °C/min, and held for 1 min; a second ramp to 280 °C was performed at a rate of 30 °C/min and held for 3 min. The total analysis time was 12 min, and the analytes were identified by the retention time.

Calibration Curves and Assay Validation. To compensate for matrix-induced effects, the mixed standard of the 10 pesticides was diluted with the blank matrix extract and then spiked with a triphenyl phosphate solution. As the components of the pickled cabbage and the brine were changing with time, the quantification of different samples was supposed to use the matrix standard solution of corresponding sampling point. Finally, a series of the matrix standard solutions (0.01, 0.1, 0.5, 1 and 2 mg/L for each pesticide, all containing triphenyl phosphate at 0.2 mg/L) were prepared at different sampling times. In all cases, peak area divided by peak area of triphenyl phosphate was used for quantification. The calibration curves were generated by plotting the ratio versus the corresponding concentration of each pesticide. The standard deviation (SD) and the relative standard deviation (RSD) ($RSD = (SD/mean) \times 100\%$) were calculated over the entire calibration range with Microsoft Excel.

The recovery experiment was also carried out at different time intervals (0, 14, 28, and 35 days). The standard solution of the OPPs was added into the blank samples of the pickled cabbage at concentrations of 0.01, 0.05, and 0.4 mg/kg, respectively ($n = 5$). The fortified concentration for the brine was 0.002, 0.02, and 0.1 mg/kg, respectively ($n = 5$). The spiked samples were extracted, purified, and analyzed according to the method mentioned above. The recovery was then calculated by comparing the concentration of each pesticide extracted from the samples with the fortified concentration. The limit of detection (LOD) for each pesticide was considered to be the concentration that produced a signal-to-noise (S/N) ratio of 3, and the limit of quantification (LOQ) was defined as S/N ratio of 10.

RESULTS AND DISCUSSION

Calibration Curves and Assay Validation. With the method mentioned above, all of the pesticides were separated simultaneously as shown in Figure 1, and there was no interference peak that might affect the analysis of the pesticides. Good linear calibrations were obtained over the concentration range of 0.01–2 mg/L for each pesticide with R^2 ranging from 0.9989 to 0.9999 and $RSD < 15\%$. However, the linear calibrations changed as time went on. For the pickled cabbage, the matrix-induced effects gradually weakened for most of the studied pesticides, whereas it presented an enhanced trend for the brine sample. The results might due to the exchange of substance between the cabbage and the brine. The mean recoveries of the 10 pesticides ranged from 76 to 102% with an RSD of 4–9% for the pickled cabbage, and for the brine it varied from 71 to 109% with an RSD of 1–12%. The LOD and LOQ are listed in Table 1. Therefore, the established methods were reliable and efficient to analyze the pesticides in the pickled cabbage and brine during the whole pickling process.

Dissipation of OPPs in the Pickled Cabbage. The reduction of the OPPs in the pickled cabbage is shown in Table 2. It was obvious that most of the OPPs were decreased when

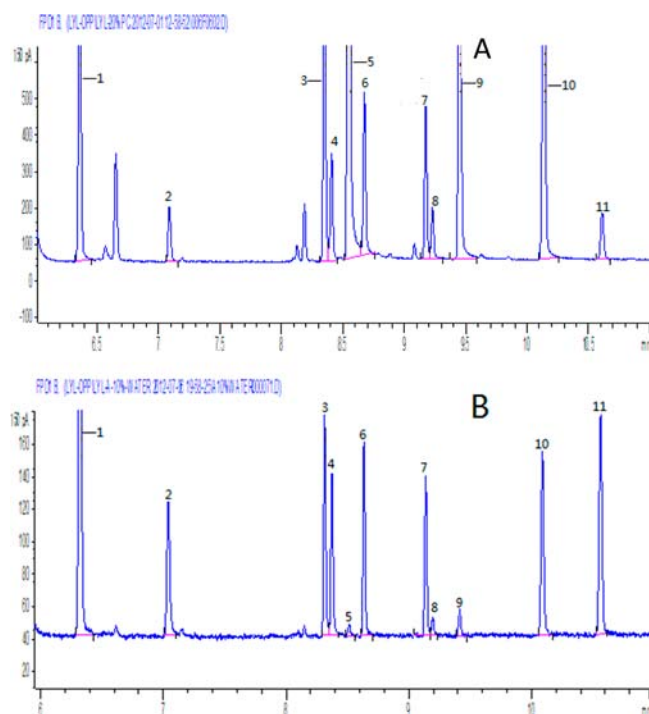


Figure 1. Representative chromatograms of extracts from (A) sample of pickled cabbage and (B) sample of brine [(1) ethoprophos, (2) dimethoate, (3) sumithion, (4) malathion, (5) chlorpyrifos, (6) isocarbophos, (7) methidathion, (8) tetrachlorvinphos, (9) profenofos, (10) triazophos, (11) triphenyl phosphate].

Table 1. Limit of Detection (LOD) and Limit of Quantification (LOQ) for the Pickled Cabbage and Brine

	brine		pickled cabbage	
	LOD (mg/kg)	LOQ (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)
ethoprophos	0.0001	0.0004	0.0005	0.0016
dimethoate	0.0006	0.0020	0.0027	0.0090
sumithion	0.0002	0.0005	0.0008	0.0026
malathion	0.0002	0.0006	0.0008	0.0027
chlorpyrifos	0.0001	0.0004	0.0006	0.0020
isocarbophos	0.0003	0.0010	0.0013	0.0044
methidathion	0.0003	0.0010	0.0014	0.0046
tetrachlorvinphos	0.0006	0.0020	0.0027	0.0090
profenofos	0.0004	0.0013	0.0018	0.0060
triazophos	0.0004	0.0013	0.0018	0.0060

the fermentation ended, but there were also some exceptions. The concentrations of chlorpyrifos in treatment C and of profenofos in treatments A and B changed slightly, and it was strange that the concentrations of chlorpyrifos and triazophos in treatment B increased up to 181.59 and 129.87%, respectively, at the last sample point. The increased concentrations might result from the loss of water in the cabbage while little of the pesticides were degraded in the process. The reductions of other pesticides were not all the same, either. Compared to the initial concentrations of these pesticides, ethoprophos, chlorpyrifos, isocarbophos, profenofos, and triazophos presented a high residue level in all treatments, whereas dimethoate, sumithion, and malathion showed a relatively low rate, and only methidathion and tetrachlorvinphos were mostly degraded. From the data on the first day, some of the pesticides rapidly disappeared, such as dimethoate,

sumithion, and malathion, whereas others did not change so much. In general, the pesticides in the cabbage behaved differently during the whole pickling process: methidathion and tetrachlorvinphos gradually dissipated, and the dynamical study showed the first-order kinetic equation was well-followed; the concentrations of ethoprophos, dimethoate, sumithion, and malathion in the cabbage decreased quickly at first and then fluctuated slightly, moving toward balance; chlorpyrifos, isocarbophos, profenofos, and triazophos showed little reduction, and the concentrations changed irregularly over the whole fermentation process. The different change trends might have certain connections with the character of the pesticides. Meanwhile, the bacteria in the pickling process played an important role in the dissipation of these pesticides, showing dissimilar biodegradation ability for different pesticides.

In this experiment, three different treatments were conducted to study the dissipation of the OPPs under different pickling methods. Statistical analysis was performed on SPSS 20.0 (Statistical Product and Service Solutions, version 20.0) to compare the differences between the three treatments. Comparisons between treatments were analyzed using one-way analysis of variance (one-way ANOVA), and a pairwise multiple-comparison procedure (LSD test) was used to compare results at $P < 0.05$. The results suggested that the concentration of NaCl and the addition of vinegar have certain influences on the dissipation of some OPPs during the pickling process. For ethoprophos, chlorpyrifos, isocarbophos, profenofos, and triazophos, treatments B and C have significant differences from treatment A ($P < 0.05$), and this indicated that higher salt content and lower pH brine resulted in the relatively low residues of these five pesticides in the pickled cabbage in treatment A. Interestingly, for sumithion, the data from treatments A and B did not show much difference, whereas there was a significant difference between treatments A and C ($P < 0.05$). This result implied that the salt content did not influence the dissipation of sumithion, but the addition of vinegar reduced the dissipation rate of sumithion in the pickled cabbage. The distinctions of each treatment might be caused by the dissimilar microorganism in the fermentation process. The character of the solution used for pickling cabbage might have an effect on the pieces and growth of the microorganism. As known to all, vinegar itself has been used as a normal bactericide, and it may subdue some bacteria at the beginning of the fermentation. Meanwhile, most bacteria and lactobacillus have the optimum pH value for growth, and the addition of vinegar lowered the pH of the brine, which might inhibit the growth of the microorganism in the pickling process.^{21,22} On the other hand, Yang had reported that high salt content would restrain the growth of LAB in the cabbage pickling process.²³ In these conditions, the reduction of the microorganism could lead to the decrease of the pesticide degradation. Nevertheless, the other pesticides (dimethoate, malathion, methidathion, and tetrachlorvinphos) had similar behaviors in the three treatments without any significant differences.

Behavior of OPPs in the Brine from Pickling. The concentrations of the OPPs in the brine were determined over the whole process, because some of the waste brine was usually poured directly into rivers or sewage systems and might cause severe pollution in the environment. As shown in Table 3, the concentrations of most OPPs in the brine reached the maximum value on the first or third day of the fermentation. However, the maximum concentration of different pesticides

Table 2. Reduction Rate (Percent) of the OPPs in the Pickled Cabbage

pesticide	treatment	0 days	1 day	3 days	5 days	7 days	14 days	21 days	28 days	35 days
ethoprophos	A	100.00	51.13	47.44	54.92	45.33	54.99	42.31	60.26	55.60
	B	100.00	68.24	77.45	83.01	93.56	90.60	83.95	69.03	92.21
	C	100.00	82.31	55.94	49.02	61.52	53.88	52.71	61.91	61.71
dimethoate	A	100.00	36.79	40.93	37.70	33.02	28.82	23.89	36.60	37.73
	B	100.00	32.43	38.66	36.80	46.66	33.28	33.60	20.82	19.67
	C	100.00	45.48	49.47	33.76	43.66	27.82	30.01	33.45	34.88
sumithion	A	100.00	40.87	19.24	16.39	14.15	14.26	14.80	28.97	22.87
	B	100.00	42.71	35.90	38.33	37.10	19.42	14.75	12.76	14.66
	C	100.00	48.99	37.54	31.49	36.30	23.02	24.34	21.70	19.21
malathion	A	100.00	35.81	27.49	25.82	20.59	18.65	14.85	23.21	18.91
	B	100.00	41.26	44.08	41.35	35.94	28.47	18.71	9.81	10.82
	C	100.00	47.14	42.54	39.27	45.69	34.78	27.46	24.13	28.67
chlorpyrifos	A	100.00	93.23	81.90	98.24	75.68	90.96	81.27	104.91	88.11
	B	100.00	129.32	141.70	173.71	135.87	146.10	144.08	133.95	181.59
	C	100.00	158.28	111.00	98.64	112.99	87.19	97.93	124.39	105.95
isocarbophos	A	100.00	60.23	54.18	54.09	36.52	47.81	34.91	71.47	81.03
	B	100.00	120.60	67.63	92.08	130.68	135.25	109.84	76.00	82.86
	C	100.00	57.39	73.96	55.55	82.05	66.59	41.34	41.84	65.34
methidathion	A	100.00	46.35	41.11	37.36	27.94	23.74	11.29	12.65	6.88
	B	100.00	51.68	48.18	46.49	32.01	18.07	9.11	3.48	1.69
	C	100.00	47.82	40.64	30.27	33.72	17.97	9.74	7.42	5.55
tetrachlorvinphos	A	100.00	39.09	31.90	27.85	18.32	19.62	16.16	25.08	16.51
	B	100.00	25.77	29.41	23.29	21.44	8.43	5.59	3.53	3.76
	C	100.00	60.58	48.45	30.30	32.44	19.72	14.13	11.32	7.75
profenofos	A	100.00	97.87	80.52	90.96	58.29	84.22	71.09	109.41	99.94
	B	100.00	103.89	126.27	139.35	110.51	124.54	98.04	83.53	104.28
	C	100.00	86.08	105.77	75.63	100.83	70.70	73.98	97.82	88.73
triazophos	A	100.00	91.65	76.44	91.73	65.11	73.72	60.06	92.60	83.32
	B	100.00	102.47	121.71	144.81	115.59	132.10	113.16	96.54	129.87
	C	100.01	79.59	72.80	69.47	73.26	66.64	65.58	74.22	71.31

varied enormously; for example, methidathion was at the maximum of 0.0457 mg/L in treatment A, whereas the maximum was 0.0007 mg/L for chlorpyrifos. This distinction was not only associated with the initial concentration of the pesticide in the cabbage but also connected with the character of each pesticide, such as the solubility in water and K_{ow} value. After the peak value, the OPPs still had different behaviors. Generally, sumithion, malathion, methidathion, tetrachlorvinphos, profenofos, and triazophos presented remarkable degradation trends, but the others fluctuated according to time, which might be caused by the exchange of these pesticides in the pickled cabbage and brine. At the end of the fermentation, almost all pesticides in each treatment were reduced to some extent, except for ethoprophos in treatment C and chlorpyrifos in treatments A and B. Nevertheless, the dissipation ratio for each pesticide was also variable, ranging from 1.47 to 84.90%. The reason might be that the microorganism in this system showed different kinetic characteristics of OPP biodegradation. Meanwhile, the stability

of these OPPs in water was also an important factor that might influence the pesticide residue level in the brine.

According to the data from Table 3, comparisons of the three treatments of each pesticide were performed on SPSS 20.0 with one-way analysis and LSD test. Obvious difference was observed on day 0, when the brine was immediately added. Other than ethoprophos, the concentrations of the rest of the OPPs were much higher in treatments B and C than in treatment A. The phenomenon was similar to the pesticide removal using different washing solutions, and it indicated that the increase of NaCl content and addition of acid enhanced the removal of the OPPs in the cabbage. This result agreed with the reports by those researchers who had studied the behavior of pesticides in vegetables and fruits during home preparation and washing process.^{9,10} For the whole pickling process, there were four types of differences between three treatments of each pesticide: (1) For tetrachlorvinphos, the residue level in all treatments did not show any difference with a P value of >0.5 . (2) For methidathion, the concentrations in treatment B was significantly different from those in treatments A and C ($P <$

Table 3. Concentrations (Milligrams per Liter) of the OPPs in the Brine on Different Days^a

pesticide	treatment	0 days	1 day	3 days	5 days	7 days	14 days	21 days	28 days	35 days
ethoprophos	A	0.0047 ± 0.0004	0.0239 ± 0.0019	0.0244 ± 0.0075	0.0384 ± 0.0007	0.0206 ± 0.0000	0.0206 ± 0.0051	0.0104 ± 0.0003	0.0208 ± 0.0004	0.0221 ± 0.0027
	B	0.0027 ± 0.0006	0.0100 ± 0.0024	0.0182 ± 0.0017	0.0136 ± 0.0007	0.0214 ± 0.0058	0.0133 ± 0.0053	0.0188 ± 0.0041	0.0153 ± 0.0022	0.0180 ± 0.0044
	C	0.0127 ± 0.0005	0.0272 ± 0.0141	0.0380 ± 0.0037	0.0252 ± 0.0064	0.0246 ± 0.0023	0.0285 ± 0.0025	0.0153 ± 0.0016	0.0153 ± 0.0017	0.0121 ± 0.0017
dimethoate	A	ND	0.0184 ± 0.0043	0.0134 ± 0.0017	0.0249 ± 0.0032	0.0148 ± 0.0040	0.0167 ± 0.0002	0.0093 ± 0.0006	0.0120 ± 0.0014	0.0107 ± 0.0036
	B	0.0040 ± 0.0005	0.0199 ± 0.0029	0.0207 ± 0.0023	0.0179 ± 0.0070	0.0270 ± 0.0022	0.0154 ± 0.0012	0.0141 ± 0.0019	0.0104 ± 0.0013	0.0107 ± 0.0025
	C	0.0114 ± 0.0030	0.0263 ± 0.0102	0.0347 ± 0.0054	0.0299 ± 0.0096	0.0229 ± 0.0021	0.0277 ± 0.0041	0.0151 ± 0.0049	0.0134 ± 0.0024	0.0134 ± 0.0024
sumithion	A	0.0016 ± 0.0006	0.0090 ± 0.0007	0.0096 ± 0.0028	0.0081 ± 0.0011	0.0064 ± 0.0006	0.0077 ± 0.0003	0.0038 ± 0.0000	0.0051 ± 0.0003	0.0034 ± 0.0003
	B	0.0049 ± 0.0007	0.0052 ± 0.0005	0.0053 ± 0.0018	0.0053 ± 0.0005	0.0047 ± 0.0029	0.0036 ± 0.0005	0.0023 ± 0.0006	0.0017 ± 0.0002	0.0019 ± 0.0003
	C	0.0189 ± 0.0030	0.0183 ± 0.0056	0.0204 ± 0.0029	0.0172 ± 0.0021	0.0142 ± 0.0016	0.0105 ± 0.0023	0.0077 ± 0.0018	0.0050 ± 0.0009	0.0050 ± 0.0009
malathion	A	0.0020 ± 0.0001	0.0105 ± 0.0014	0.0090 ± 0.0014	0.0119 ± 0.0006	0.0082 ± 0.0004	0.0079 ± 0.0002	0.0043 ± 0.0002	0.0058 ± 0.0005	0.0045 ± 0.0001
	B	0.0062 ± 0.0006	0.0088 ± 0.0014	0.0109 ± 0.0014	0.0074 ± 0.0016	0.0051 ± 0.0023	0.0041 ± 0.0003	0.0034 ± 0.0002	0.0022 ± 0.0002	0.0026 ± 0.0006
	C	0.0171 ± 0.0028	0.0199 ± 0.0041	0.0216 ± 0.0029	0.0199 ± 0.0029	0.0130 ± 0.0029	0.0133 ± 0.0009	0.0073 ± 0.0026	0.0052 ± 0.0002	0.0052 ± 0.0002
chlorpyrifos	A	ND	ND	0.0007 ± 0.0003	0.0005 ± 0.0001	0.0006 ± 0.0002	0.0007 ± 0.0002	0.0005 ± 0.0001	ND	0.0007 ± 0.0000
	B	0.0006 ± 0.0001	0.0005 ± 0.0000	0.0005 ± 0.0001	0.0005 ± 0.0000	0.0006 ± 0.0001	0.0006 ± 0.0001	0.0006 ± 0.0001	0.0007 ± 0.0001	ND
	C	0.0015 ± 0.0001	0.0013 ± 0.0004	0.0014 ± 0.0001	0.0008 ± 0.0001	0.0012 ± 0.0001	0.0008 ± 0.0000	0.0007 ± 0.0000	0.0007 ± 0.0000	0.0008 ± 0.0001
isocarbophos	A	0.0015 ± 0.0004	0.0208 ± 0.0062	0.0206 ± 0.0002	0.0401 ± 0.0022	0.0297 ± 0.0025	0.0261 ± 0.0009	0.0145 ± 0.0011	0.0226 ± 0.0041	0.0205 ± 0.0016
	B	0.0095 ± 0.0015	0.0218 ± 0.0044	0.0410 ± 0.0027	0.0226 ± 0.0069	0.0130 ± 0.0067	0.0101 ± 0.0016	0.0177 ± 0.0005	0.0151 ± 0.0034	0.0239 ± 0.0093
	C	0.0161 ± 0.0046	0.0374 ± 0.0130	0.0545 ± 0.0039	0.0578 ± 0.0108	0.0461 ± 0.0081	0.0556 ± 0.0068	0.0268 ± 0.0085	0.0242 ± 0.0025	0.0491 ± 0.0080
methidathion	A	0.0032 ± 0.0015	0.0457 ± 0.0081	0.0218 ± 0.0030	0.0315 ± 0.0013	0.0181 ± 0.0006	0.0170 ± 0.0004	0.0045 ± 0.0001	0.0033 ± 0.0001	0.0020 ± 0.0002
	B	0.0060 ± 0.0006	0.0204 ± 0.0007	0.0195 ± 0.0035	0.0133 ± 0.0045	0.0078 ± 0.0038	0.0043 ± 0.0006	0.0017 ± 0.0002	ND	ND
	C	0.0202 ± 0.0056	0.0339 ± 0.0104	0.0369 ± 0.0049	0.0326 ± 0.0074	0.0178 ± 0.0030	0.0104 ± 0.0013	0.0051 ± 0.0011	0.0031 ± 0.0004	0.0028 ± 0.0004
tetrachlorvinphos	A	0.0030 ± 0.0013	0.0285 ± 0.0042	0.0139 ± 0.0041	0.0156 ± 0.0009	0.0088 ± 0.0000	0.0093 ± 0.0003	0.0027 ± 0.0003	0.0028 ± 0.0003	0.0024 ± 0.0002
	B	0.0074 ± 0.0008	0.0131 ± 0.0021	0.0110 ± 0.0012	0.0115 ± 0.0027	0.0059 ± 0.0016	0.0052 ± 0.0030	0.0022 ± 0.0008	0.0030 ± 0.0004	0.0034 ± 0.0014
	C	0.0165 ± 0.0042	0.0165 ± 0.0031	0.0148 ± 0.0005	0.0117 ± 0.0019	0.0070 ± 0.0018	0.0044 ± 0.0006	0.0036 ± 0.0005	ND	ND
profenofos	A	ND	ND	0.0043 ± 0.0017	0.0038 ± 0.0006	0.0046 ± 0.0008	0.0046 ± 0.0007	0.0021 ± 0.0000	0.0025 ± 0.0002	0.0020 ± 0.0001
	B	0.0055 ± 0.0008	0.0047 ± 0.0004	0.0042 ± 0.0005	0.0054 ± 0.0002	0.0044 ± 0.0012	0.0028 ± 0.0009	0.0021 ± 0.0003	0.0015 ± 0.0004	ND
	C	0.0118 ± 0.0021	0.0108 ± 0.0012	0.0091 ± 0.0009	0.0072 ± 0.0011	0.0066 ± 0.0015	0.0050 ± 0.0004	0.0063 ± 0.0022	0.0041 ± 0.0004	0.0035 ± 0.0007
triazophos	A	0.0046 ± 0.0015	0.0284 ± 0.0034	0.0143 ± 0.0029	0.0209 ± 0.0025	0.0143 ± 0.0033	0.0165 ± 0.0009	0.0090 ± 0.0007	0.0097 ± 0.0006	0.0095 ± 0.0007
	B	0.0069 ± 0.0007	0.0106 ± 0.0024	0.0103 ± 0.0011	0.0092 ± 0.0012	0.0067 ± 0.0030	0.0078 ± 0.0006	0.0067 ± 0.0004	0.0065 ± 0.0005	0.0066 ± 0.0011
	C	0.0198 ± 0.0018	0.0306 ± 0.0055	0.0298 ± 0.0027	0.0284 ± 0.0035	0.0196 ± 0.0043	0.0202 ± 0.0017	0.0156 ± 0.0065	0.0116 ± 0.0008	0.0220 ± 0.0064

^aND, no detection.

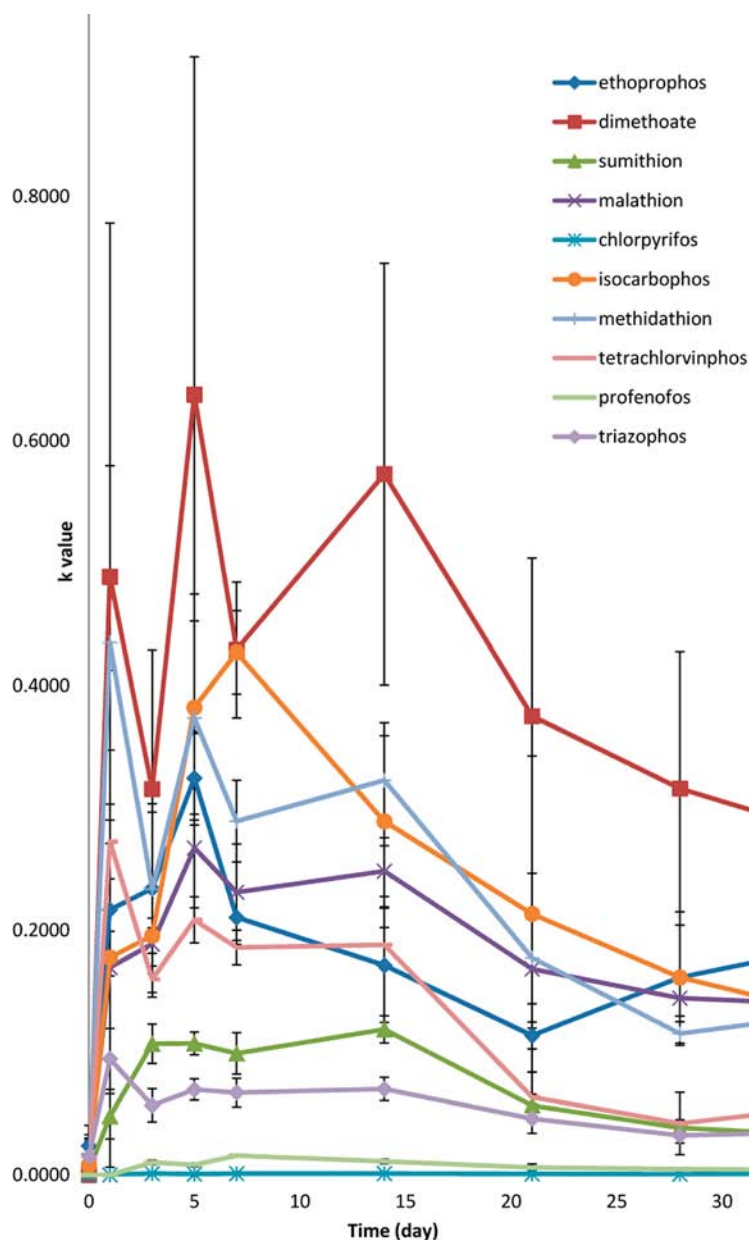


Figure 2. *k* value of each pesticide in treatment A during the cabbage pickling process.

0.05), resulting in a lower residue level in treatment B, whereas there was no difference between treatments A and C. (3) The statistical results of dimethoate, malathion, isocarbophos, and profenofos represented that treatments A and B were similar ($P > 0.05$), but treatment C was obviously different from both treatments A and B ($P < 0.05$). It was observed that the residue level of the four pesticides was higher in treatment C than that in treatments A and B during the whole process. (4) There was significant difference between each treatment for the rest of the OPPs (ethoprophos, sumithion, chlorpyrifos, and triazophos, $P < 0.05$). These results meant that the change of salt content and pH value would influence the residues in the brine.

In addition, except for tetrachlorvinphos, all of the other OPPs exhibited a high residue level in treatment C, and there were several factors that might contribute to this result. First, most of the OPPs showed better stability in the acid matrix than others. Second, the addition of vinegar might accelerate the release of the OPPs from the solid phase to the liquid

phase. Another reason might be that the lower pH of the brine caused the reduction of microorganisms or the decrease of their activity, which slowed the degradation rate of the OPPs. The interaction of these factors eventually led to high pesticide residue levels in treatment C.

Comparison of the Residues in the Brine and Cabbage. From the result above, we could find that the OPPs redistributed in brine and cabbage during the pickling procedure. Compared by concentration, the residues of the 10 pesticides were higher in the pickled cabbage than in the brine. Nevertheless, this did not mean that there was lower levels of residues in the brine, because the mass of the brine was over twice that of the cabbage, and the water loss of the pickled cabbage might increase the concentration of the OPPs in the cabbage. Especially for dimethoate, the mass of the residue was greater in the brine than in the cabbage, which might be related with its good solubility in water (23.3 g/L). From the data of the first few days, it could be found that there were some

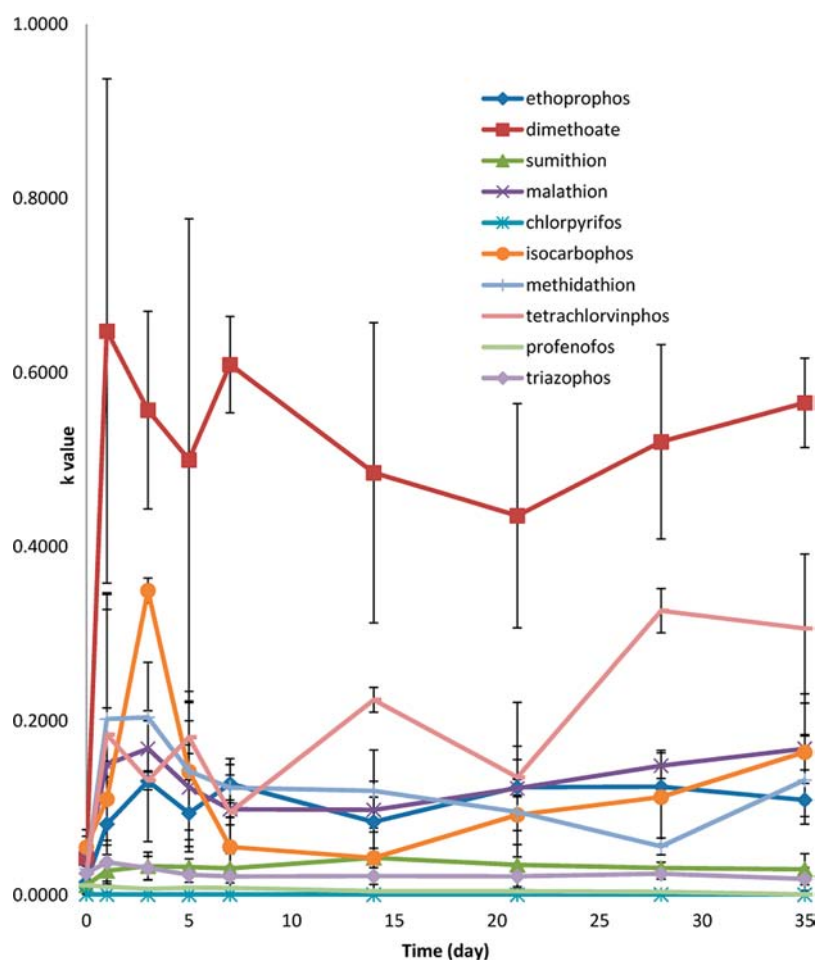


Figure 3. k value of each pesticide in treatment B during the cabbage pickling process.

connections between the decrease of the residues in the cabbage and the increase of the residues in the brine. This indicated that the rapid residue dissipation in the cabbage was mainly attributed to the washing function of the brine and the dissipation in the following days mainly to the action of the microorganism.

To evaluate the distribute pattern in the pickling process, the partition coefficient was calculated by eq 1, where k is the partition coefficient, C_1 is the concentration of the OPPs in the brine, and C_2 is the concentration of OPPs in the cabbage samples.

$$k = C_1/C_2 \quad (1)$$

Figures 2–4 showed the change of k values during the cabbage pickling process in each treatment. From the figures, it was obvious that k values of different pesticides were at dissimilar levels, although it changed with time. Among the 10 pesticides, chlorpyrifos showed the minimum k value in all treatments, whereas the k value of dimethoate was relatively larger than others. The solubility of pesticide might be the main factor that caused the differences. Generally, there were three kinds of changing mode of the 10 pesticides in all treatments, and it could be concluded as “increase–decrease”, “increase–decrease–balance”, and “increase–decrease–increase”. On this basis, these pesticides were classified in Table 4. In the first step, all of the OPPs behaved in an increasing trend, which was due to the transformation of the OPPs from the cabbage to the brine. After the peak value, a decrease process was observed,

which meant that the concentration of the OPPs in the brine was lessened more quickly than that in the cabbage. However, because of the exchange of OPPs between the cabbage and brine, the k values were in equilibrium for most pesticides at the end of the fermentation.

To analyze the differences between treatments, statistical analysis was performed, and some general laws were discovered. For dimethoate, chlorpyrifos, and profenofos, the partition patterns were similar in treatments A and B, whereas it was peculiar in treatment C with a higher k value. For ethoprophos, sumithion, methidathion, tetrachlorvinphos, and triazophos, there was no differences between treatments A and C, whereas treatment B was significantly different from treatments A and C. The k values of these OPPs were smaller in treatment B than in treatments A and C except for tetrachlorvinphos, which had a larger k value. The trends of malathion and isocarbophos were all different in the three treatments; the k value of treatment C was the largest, and the k value of treatment B was the smallest in the three treatments. The data of partition coefficient afforded a good means of predicting the potential risk in foods and the environment.

The data obtained in this experiment would add to the understanding of the behavior of OPPs during the cabbage pickling process and are also useful in industrial production. The residues of chlorpyrifos and triazophos on cabbages used for pickling should be strictly controlled, because the concentration of such pesticides might increase and be higher than the initial concentration, which might lead to acute

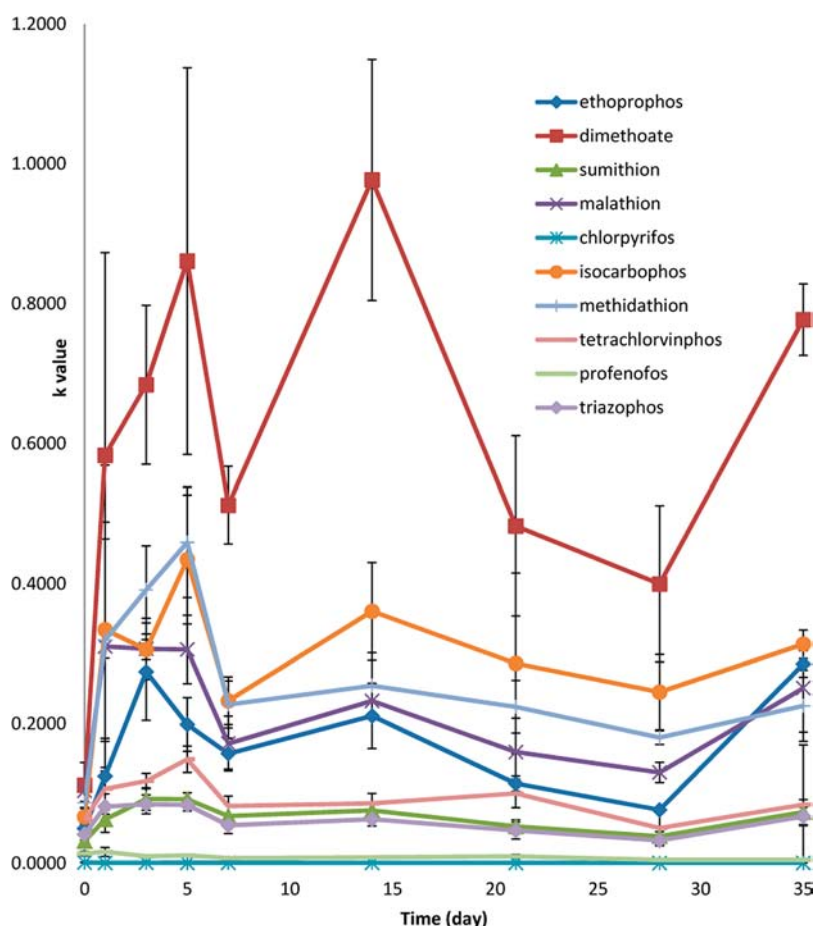


Figure 4. k value of each pesticide in treatment C during the cabbage pickling process.

Table 4. Classification of the OPPs by the Change Mode of k value

	treatment A	treatment B	treatment C
“increase–decrease” mode	dimethoate, isocarbophos, malathion		
“increase–decrease–balance” mode	chlorpyrifos, profenofos, triazophos, sumithion, tetrachlorvinphos	chlorpyrifos, profenofos, triazophos, sumithion, dimethoate, ethoprophos,	chlorpyrifos, profenofos, triazophos, sumithion, tetrachlorvinphos, methidathion, isocarbophos,
“increase–decrease–increase” mode	ethoprophos, methidathion	isocarbophos, methidathion, tetrachlorvinphos, malathion	ethoprophos, malathion, dimethoate

intoxication. On the other hand, the industrial brine from the pickling process might contain some highly toxic pesticides (such as ethoprophos and dimethoate) from the raw material cabbages, so it should be clarified before being released into the environment. The pickling solution would influence the behavior of the OPPs during this fermentation process, so if the pesticide residue on the cabbage was known, the proper pickling solution might be chosen to reduce the pesticide residues in the final product.

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