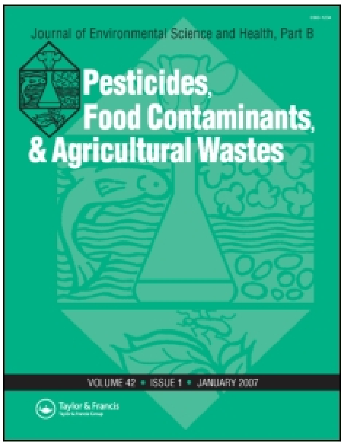

Journal of Environmental Science and Health, Part B
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597269

Dissipation of carbofuran and carbaryl on Oolong tea during tea bushes, manufacturing and roasting processes

Chia-Chang Wu [a]; Chun Chu [b]; Yei-Shung Wang [c]; Huu-Sheng Lur [b]
[a] Tea Research Extension Station, Nantou, Taiwan [b] Department of Agronomy, National Taiwan University, Taipei, Taiwan [c] Department of Agricultural Chemistry, National Taiwan University, Taipei, Taiwan

To cite this Article Wu, Chia-Chang, Chu, Chun, Wang, Yei-Shung and Lur, Huu-Sheng'Dissipation of carbofuran and carbaryl on Oolong tea during tea bushes, manufacturing and roasting processes', Journal of Environmental Science and Health, Part B, 42: 6, 669 — 675

To link to this Article: DOI: 10.1080/03601230701465783

URL: http://dx.doi.org/10.1080/03601230701465783

Journal of Environmental Science and Health Part B (2007) **42**, 669–675
Copyright © Taylor & Francis Group, LLC
ISSN: 0360-1234 (Print); 1532-4109 (Online)
DOI: 10.1080/03601230701465783

Taylor & Francis
Taylor & Francis Group

Dissipation of carbofuran and carbaryl on Oolong tea during tea bushes, manufacturing and roasting processes

CHIA-CHANG WU[1], CHUN CHU[2], YEI-SHUNG WANG[3] and HUU-SHENG LUR[2]

[1] *Tea Research Extension Station, Nantou, Taiwan*
[2] *Department of Agronomy, National Taiwan University, Taipei, Taiwan*
[3] *Department of Agricultural Chemistry, National Taiwan University, Taipei, Taiwan*

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranol-N-methylcarbamate) and carbaryl (1-naphthyl-N-methylcarbamate) are insecticides widely used in tea plantations. The objective of the present study was to evaluate the dissipation of carbofuran and carbaryl during the growth periods of Oolong tea, processing and roasting. Analysis of the residual insecticides was carried out using high-pressure liquid chromatography with a post-column fluorescence detector. Results showed that in the tea field carbofuran dissipated faster then carbaryl. Manufacturing processes of Oolong tea further reduced the carbofuran and carbaryl contents. The persistence of carbofuran and carbaryl was decreased with increasing roasting temperature. From the results, we conclude that the presence of carbofuran and carbaryl in tea can be reduced by proper field management, manufacturing and roasting processes.

Keywords: Carbofuran; carbaryl; tea; manufacture.

Introduction

The climate and natural environment in many regions of Taiwan are suitable for tea cultivation and production. The tea plant, *Camellia sinensis* (L.) O. Kuntze, is a major crop in Taiwan, and tea is the most widely consumed beverage in the world, because of its characteristic aroma, flavor and health benefits. Taiwan is one of the world-famous places producing Oolong tea. As with most other crops, pesticides play an important role in tea cultivation to control diseases, pests and weeds, because the pesticides produce rapid and reliable results and are easy to use. Hence, the use of pesticides remains one of the most important control measures for tea plant protection. However, due to their high toxicity and widespread use in agricultural areas, residues from pesticides application should be monitored in the environment.

In recent years, there is an increasing public concern over the presence of pesticide residues in food products because of the known toxicity of pesticides,[1–2] and tea is no exception.[3] Consumers have begun to question how tea is produced and what it contains since they no longer accept that the tea available on market shelves is necessarily safe. Therefore, the use of pesticides in tea plantations and the consequent presence of pesticide residues in tea products have been receiving remarkable public awareness.[1,4] To prevent health problems for consumers, various international authorities have regulated the use of pesticides by fixing maximum residues levels (MRLs) for commercial purposes.[5] For the time being importing countries are free to maintain or set their own tentative limits. As a result of the existing inconsistencies in standards, problems with the global tea trade are arising.

Carbofuran (2,3-dihydro-2,2-dimethyl-7-benzofuranol-N-methylcarbamate) and carbaryl (1-naphthyl-N-methylcarbamate) are insecticides widely used in tea plantation to control insects such as Jacobiasca formosana (Paoli), smaller green leaf-hopper; Andraca bipunctata walker, cluster caterpillar; Euproctis pseudoconspersa (strand), tea tussock moth; Eumeta minuscula (butler), tea bag worm; Orgyia Postica (walker), and the small tussock moth.[6] The dissipation of these two insecticides in the tea field and manufacture processes, nevertheless, has not been documented. From May 25, 2006, Taiwan tea exports to Japan were required to abide by the new rules of pesticide residue inspection for Japan. The Council of Agriculture found that the MRLs of carbaryl and carbofuran in Taiwan (1.0 mg kg^{-1} and 0.2 mg kg^{-1}) are two to five times higher than the Japanese limits (2.0 mg kg^{-1} and 1.0 mg kg^{-1}).[5]

This study was undertaken to investigate the behavior of carbofuran and carbaryl on tea bushes and their

---

Address correspondence to Huu-Sheng Lur, Department of Agriculture, National Taiwan University, Taipei, Taiwan; Phone: +886-2-33664773; Fax: +886-2-2620879; E-mail: lursh@ntu.edu.tw, lurhs@ntu.edu.tw
Received March 8, 2007.

degradation during manufacture and roasting processing. This knowledge is vital to help tea farmers to establish consistent safety controls for tea, achieve safe tea and ensure worry-free tea consumption. The study is also important for the benchmark establishment among international standards.

Materials and methods

Field trials

Field trials were carried out at the Song-hui tea garden of Mingjan Township (Nantou, Taiwan) in July, 2005. A random block design was used, each block containing 15 plants of Ching-Shing Oolong that were 10 years of age. The experimental plots (around 0.2 ha each) were assigned for different pesticides and application rates. Each block was partitioned and isolated from one another by leaving one untreated row as guard row to prevent pesticide spill-over.

Carbofuran (40.6% SC) was sprayed at two rates, 0.80 L ha^{-1} (recommended) and 1.60 L ha^{-1}(double of the recommended), in four replications, and carbaryl (39.5% WP) was sprayed at two rates, 1.25 kg ha^{-1} (recommended) and 2.50 kg ha^{-1} (double of the recommended), in four replications. In control blocks only water was sprayed.

Pesticides dissipation studies

Field experiment

About 0.5 kg of the green tea shoots (with two leaves and apical bud) was harvested from each replicate of the treated and control plots and brought to the laboratory for analysis. The leaves were harvested at the following times: 0 (1 hour after spraying), 1, 3, 6, 9, 12, 15, 18, 21, 24, 27 and 30 days after spraying.

Manufacturing of tea

In normal tea manufacturing, the leaves are harvested at 7–21 days after the application of pesticides. However, in determining the dissipation of the pesticides of the present study, the sampling was done 24 hours after spraying to allow maximum possible assimilation of pesticide by the plants. About 50 kg of the green shoots (with two leaves and a bud) is harvested for normal tea manufacture processing. The normal manufacture procedure of Oolong tea in Taiwan was described in Table 1.

Roasting of tea

To analyze dissipation during roasting, the primary made tea treated with carbofuran and carbaryl was roasted under four temperatures (70°C, 100°C, 130°C and 160°C) and sampled at six time intervals (from 1 to 6 hour). Each sample dish in the roasting machine contained 1 kg of the primary made tea treated with pesticides.

Calculation of degradation percentage

In the degradation study, the degradation percentage was calculated according to following formula. Degradation (%) $= ((C_o - C_t)/C_o) \times 100$. In the tea manufacturing processing experiment, C_o referred to the pesticides concentration in fresh tea leaves; and C_t represented the pesticides concentration that remained in each manufacturing processing stage. As in the tea roasting processing experiment, C_o referred to the pesticides concentration in primary made tea; and C_t represented the pesticides concentration remained in each roasting processing stage.

Sample preparation

For field samples ten grams of fresh tea leaves were extracted with 100 mL acetonitrile by homogenization for 1 min with the polytron. For manufacturing primary-made

Table 1. Processing stages for Oolong tea.

Stage	*Treatment*
A: Fresh tea leaves	Fresh tea leaves (two or three leaves and buds) are plucked by hand.
B: Solar withering	The leaves are spread to a thickness of 1 kg per square meter. The time for solar withering is 30 min, yielding a weight loss of 20% of the original weight of fresh tea leaf.
C,D,E: Indoor sitting and shaking (1st,2nd,3rd)	Withered tea leaves are allowed to sit for 1 hour before the 1st shaking with the leaves spread tea thickness of 7–10 cm. The 1st shaking is 5 min, followed by sitting for 2 hrs. The 2nd shaking is also 5 min, followed by sitting for 2 hrs. The third shaking is 15 min, and the tea leaves are then left to sit for 4 hrs with a thickness of 13–15 cm. The total time is eight hours.
F,G: Panning (Before, After)	Panning is conducted in a slanted pan, the panning temperature between 180–220°F, and lasts for 8–10 min until the tea leaf is soft and sticky to the hands, and the greenish odor has changed to a pleasant aroma.
H: Rolling	After the primary panning, tea leaves are transferred to the roller for 10 mins rolling. Leaf juice is leached out as the tea leaves are rolled to a stringy shape.
I: Primary drying	The rolled leaves are then dried in a drier using hot air at 95–100°C for 20 min.
J,K: Ball rolling (Before, After)	Using ball roller machine for 15 min, the leaves are made into semispherical balls.
L: Primary made tea (Secondly drying)	The ball-rolled leaves are then dried in a drier using hot air at 95–100°C for 20 min.

tea samples (10 g) were immersed in 40 mL distilled water for 20 min and extracted with 100 mL acetonitrile by homogenization for 1 min with the polytron. Extracts were filtered through a Whatman GF/C 110 mm filter paper with vacuum pump, after transfer to flask then add acetonitrile to 200 mL. Immediately after addition of 15 g NaCl and shaking for 1 min, the upper 10 mL of the acetonitrile layer were collected, and evaporated to dryness with nitrogen gas. The residue was then dissolved in acetonitrile.

Chemicals

All analytical standards including carbofuran (CAS-No 1563-66-2, $C_{12}H_{15}NO_3$, 99.9%), and carbaryl (CAS-No 63-25-2, $C_{12}H_{11}NO_2$, 99.8%) were obtained from Riedel-de Haen, USA. A standard stock solution (1000 mg L^{-1}) was prepared in acetonitrile and stored at −20°C. The working solutions required for preparing a standard curve (0.1, 0.5, 1.0, 2.5 and 5.0 mg mL^{-1}) were prepared daily from the standard stock solution by serial dilutions. All the solvents and chemicals used in this study were of analytical grade from Merck (Germany).

Apparatus and chromatographic conditions

Carbofuran and carbaryl were determined using high-pressure liquid chromatography (HPLC) and a post-column fluorescence system. This system consisted of an Agilent 1100 series liquid chromatograph system (Agilent Technologies, USA), including a fluorescence detector used to quantify carbofuran and carbaryl derivatives, a vacuum solvent degassing unit, a binary high-pressure gradient pump, an automatic sample injector, a column thermostat and a deliver reactor.

The post-column reactor utilized sodium hydroxide and o-phthalaldehyde/thiofluor reagents which were delivered at 100°C by the pumps in the Pickering model PCX 5100X module. The resulting fluorescent derivative was analyzed using an excitation wavelength of 330 nm and an emission wavelength of 460 nm.

The separation of carbofuran and carbaryl in all the experiments was carried out using a C18, 5 μM spherical column (4.6 × 250 mm, Astec, USA). The column was maintained at a constant temperature of 42°C. The HPLC flow rate was set at 10 μL min^{-1}, utilizing a linear gradient mobile phase of water—acetonitrile (initial from 75/25 to 60/40 at 5 min, 60/40 to 40/60 at 10 min, 40/60 to 25/75 at 15 min, then to 0/100 at 20 min. The chromatograms for the separation of the mixture of standard pesticides (carbofuran and carbaryl) in the treated field tea sample, manufactured tea sample, roasted sample, and untreated control sample are illustrated as Figure 1. The retention time of carbofuran and carbaryl were 11.36 and 12.01 min, respectively.

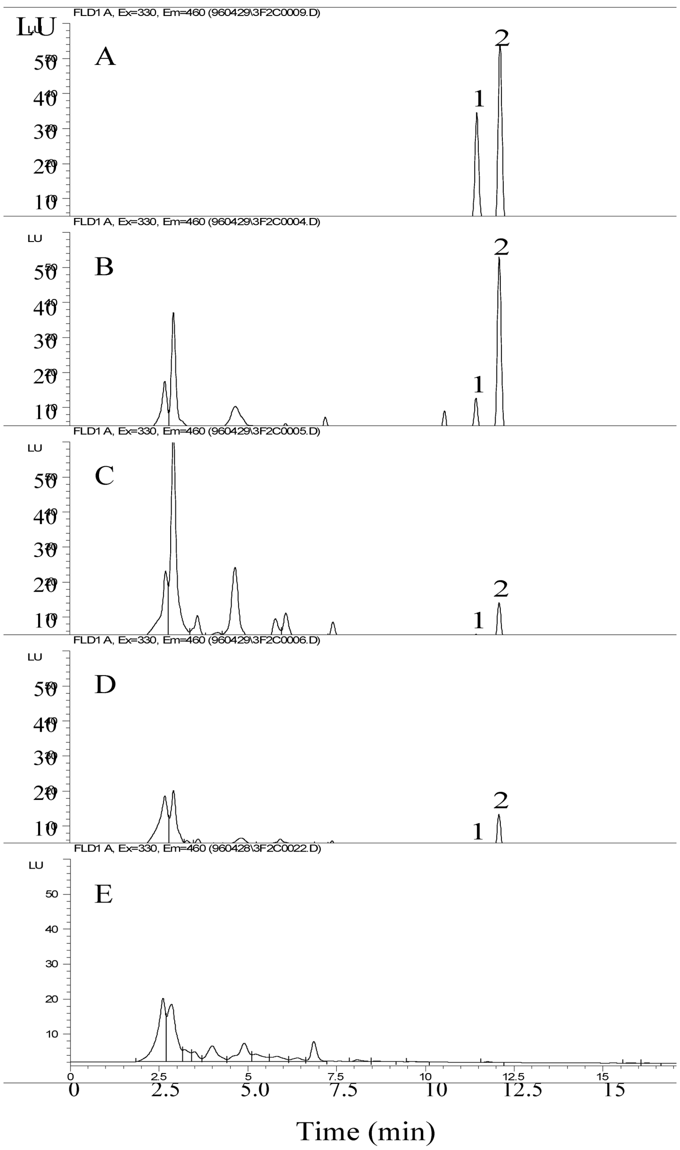

Fig. 1. Chromatograms for: (a) standard mixture of pesticides 5 mg kg^{-1}, peak (retention time, min):1 = carbofuran (11.36) and 2 = carbaryl (12.01); (b) treated field tea sample; (c) treated manufacture tea sample; (d) treated roasted sample; and (e) untreated control sample. Analysis condition is explained in "Apparatus and Chromatographic Conditions" section.

Detection and quantification

Quantification of carbofuran and carbaryl were accomplished using a standard curve prepared by diluting the stock solution in acetonitrile. Good linearity was achieved between the ranges 0.1–5.0 mg kg^{-1} with a correlation coefficient of 0.99. Recovery tests were performed in triplicate by spiking standards at 1.0 mg kg^{-1} into samples. The spiked samples and blank samples without standard were then analyzed by HPLC. Recovery was determined by comparing the amount of pesticides added with the amount of pesticides recovered. Recoveries of carbofuran and carbaryl were 111.97% and 117.95%, respectively. Limits of detection were based on a signal to noise (S/N) ratio with 3:1 as the minimum. Limits of detection were 0.004 and 0.007 mg kg^{-1} for carbofuran and carbaryl, respectively.

Results and discussion

Dissipation in fresh tea leaves in the field

Several studies have addressed the dissipation of carbofuran, carbaryl and their metabolites in soil, water, and crop plants.[7–10] Nevertheless, in tea the information related to the degradations and metabolites of carbofuran and carbaryl is still unclear. In the present study, the levels of main degradation products, e.g. 3-hydroxy carbofuran, 3-keto carbofuran and 1-naphthol were too low to be detected. Thus, the amounts of carbofuran and carbaryl of tea samples were measured and used for calculating the change of degradation percentage. Examples of HPLC chromatograms for chemical standards in treated field tea sample, manufactured sample, roasted sample, and untreated control sample are shown as Figure 1. The residual level of carbofuran and carbaryl in fresh tea leaves at the recommended and double the recommended application rates at different harvest intervals are presented in Table 2. The application rates of carbofuran in field green tea shots were 0.80 L ha^{-1} (recommended) and 1.60 L ha^{-1} (double of the recommended), and the initial deposits were 12.42 and 45.52 mg kg^{-1}, respectively. Carbaryl was applied at two rates 1.25 kg ha^{-1} (recommended) and 2.50 kg ha^{-1} (double of the recommended), the initial deposits were 23.41 and 76.72 mg kg^{-1}, respectively. Since the spraying was done on the crop in different blocks, due to differential density of canopy and manual field operations empirical values may not be a simple arithmetic multiplication of the residue level at two different concentrations. Six days after the carbofuran applications (recommended and double of the recommended) the residues observed in fresh tea leaves were 2.05 and 2.47 mg kg^{-1} sprayed at the two rates, respectively. The persistence of carbofuran was found between 4.02 and 5.56% in fresh tea leaves. On the ninth day after carbaryl application the residues were 4.55 and 5.31% in fresh tea leaves, respectively.

The residue values presented in Table 2 reveal that no measurable amount of carbofuran residues was observed after 15 days after treatment for either recommended or double of the recommended application rates. And no measurable residue of carbaryl was found after 15 days and 21 days after treatment with recommended and double of the recommended doses, respectively.

The dissipation rate of fresh tea leaves exhibited a first order kinetics. The half-life of carbofuran calculated in fresh tea leaves treated at recommended and double of the recommended doses was 2.35 days and 1.65 days respectively (Table 2). The calculated half-life for carbaryl in fresh tea leaves were 1.80 days and 2.08 days, respectively. This indicated slightly faster residue dissipation of carbofuran then carbaryl at fresh tea leaves in field. For comparison with other crops, in strawberries and tomatoes, the half-life of carbaryl are 4.10 days[11] and 1.40 days,[12] respectively. In strawberries the half-life value of carbofuran is 3.10 days.[13] The more rapid breakdown of carbofuran then carbaryl under tea field conditions can be recognized as a desirable chemical characteristic. Differences between residues of carbofuran and carbaryl on fresh tea leaves are due to the different physical and chemical properties of pesticides. In addition, the apparent persistence of pesticide residues on the leaves and other parts, because pesticides diluted by

Table 2. Degradation of carbofuran and carbaryl residues in the tea field

	Residues (mg/ kg)			
	Carbofuran		*Carbaryll*	
Elapsed time after treatment (days)	*Trt. 1*	*Trt. 2*	*Trt. 3*	*Trt. 4*
0	44.52 ± 0.51 (0.00)[a]	12.42 ± 0.55 (0.00)	76.72 ± 0.63 (0.00)	23.41 ± 0.17 (0.00)
3	19.12 ± 0.15 (56.96)	3.53 ± 0.45 (70.85)	32.10 ± 0.19 (58.10)	13.75 ± 0.47 (32.30)
6	2.47 ± 0.19 (94.46)	2.05 ± 0.49 (90.61)	10.38 ± 0.23 (86.46)	5.75 ± 0.42 (77.19)
9	1.03 ± 0.09 (97.68)	0.39 ± 0.19 (96.25)	4.08 ± 0.17 (94.69)	0.85 ± 0.23 (95.45)
12	0.35 ± 0.05 (99.21)	0.45 ± 0.19 (94.99)	1.22 ± 0.06 (98.41)	0.30 ± 0.14 (97.91)
15	ND	ND	0.41 ± 0.07 (99.46)	ND
18	ND	ND	0.26 ± 0.04 (99.67)	ND
21	ND	ND	ND	ND
24	ND	ND	ND	ND
27	ND	ND	ND	ND
30	ND	ND	ND	ND
Half life, days	1.65	2.35	2.08	1.80

Carbofuran: Trt.1, treatment No. 1 (spray at 0.80 L ha^{-1}); Trt. 2, treatment No. 2 (spray at 1.60 L ha^{-1}); Carbaryl: Trt. 3, treatment No. 1 (spray at 1.25 Kg ha^{-1}); Trt. 4, treatment No. 2 (spray at 2.50 Kg ha^{-1}); a: Degradation % in parenthesis; ND: Not detected; Data are the means ± SE of three replicates.

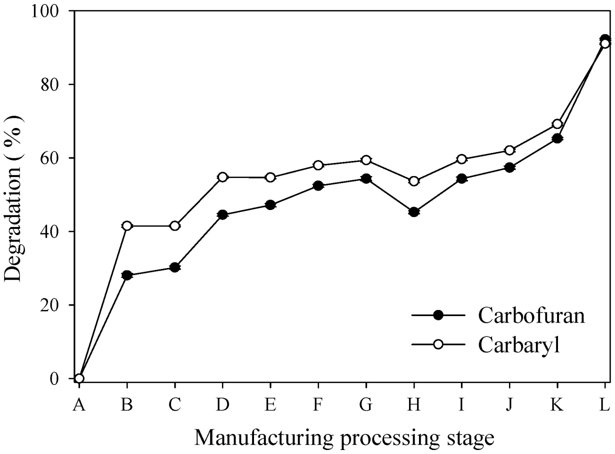

Fig. 2. Disappearance of carbofuran and carbaryl at different Oolong tea manufacturing processing stages. Processing stages: a) Fresh tea leaves; b) Solar withering; c) 1st indoor sitting and shaking ; d) 2nd indoor sitting and shaking; e) 3rd indoor sitting and shaking; f) before panning; g) after panning; h) rolling; i) primary drying; j) before ball rolling; k) after ball rolling; l) primary made tea (secondly drying). Data are the means ± SE of three replicates.

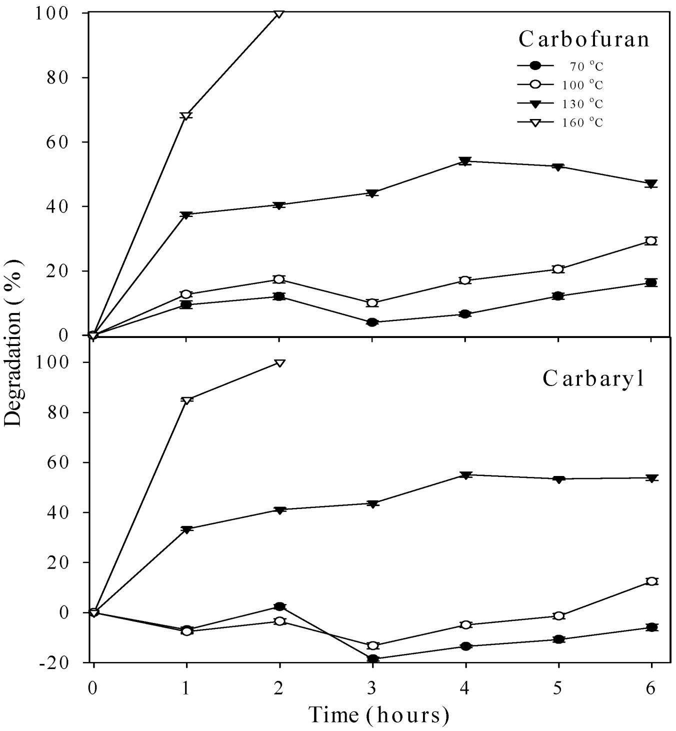

Fig. 3. Disappearance of carbofuran and carbaryl at different roasting temperatures and times. Data are the means ± SE of three replicates.

a greater surface area as the tea plant grows.[14] Other factors affecting pesticide degradation rates are temperature and moisture.[15] Furthermore, the volatility after pesticide application can result in a significant loss of residues from treated surfaces, with the rate of volatilization directly related to the input of solar radiation.[16]

Dissipation in tea manufacture processing

Heavy use of pesticides on field crops has received much attention, and many researchers have studied how to remove or reduce pesticides in agricultural products.[17–20] It is, therefore, important to know how much carbofuran and carbaryl degrade during the tea manufacture processing stages. The results revealed that the carbofuran contents in fresh tea leaves reduced by 28.04% after 30 min solar withering (Fig. 2). There was no significant difference between the solar withering stage and 1st indoor sitting and shaking stage. Even though the tea leaves were prepared in the panning machine for 10 min, with the pan surface temperature at 160–180°C, decreased only 54.34% of the carbofuran. After the ball rolling stage, carbofuran was degraded by 65.24%. In the final stage the detected carbofuran residues decreased to only 7.77 % (0.25 mg kg^{-1}).

For the carbaryl of tea manufacture processing experiment, carbaryl residues had reduced by 41.47% in fresh tea leaves after 30 min solar withering (Fig. 2). At the 2nd indoor sitting and shaking stage, carbaryl degradation was 54.74%. Before the ball rolling stage, only 38.02% carbaryl was left in the tea leaves. Carbaryl was significantly decreased in the primary made tea stage, and there was only 8.98 % (1.21 mg kg^{-1}) could be detected in final stage. The findings show that for Oolong tea, the processing steps significantly reduced the carbofuran and carbaryl contents. Similar results have been reported in green tea and black tea manufacturing processes.[21–22] The different degradation rates of carbofuran and carbaryl may be attributed

Table 3. Kinetic parameters for the degradation of carbofuran at different roasting temperatures and times

Roasting temperatures	*Equation of first order kinetics*	*Correlation coef. squared (R^2)*	*Rate constant k (hours)$^{-1}$*	*Half-life $t_{1/2}$ (hours)*
70°C	$C = 1.13e^{-0.0194t}$	0.4360	0.0194	35.70
100°C	$C = 1.13e^{-0.0488t}$	0.8383	0.0488	14.20
130°C	$C = 1.13e^{-0.0989t}$	0.6583	0.0989	7.20
160°C	$C = 1.13e^{-1.2124t}$	0.9993	1.2124	0.57

C: Concentration (mg kg $^{-1}$) of carbofuran residues.

Table 4. Kinetic parameters for the degradation of carbaryl at different roasting temperatures and times

Roasting temperatures	*Equation of first order kinetics*	*Correlation coef. squared (R^2)*	*Rate constant k (hours)$^{-1}$*	*Half-life $t_{1/2}$ (hours)*
70°C	$C = 6.35e^{0.0130t}$	0.1614	- 0.0130	—
100°C	$C = 6.35e^{-0.0153t}$	0.1859	0.0153	45.30
130°C	$C = 6.35e^{-0.1201t}$	0.8111	0.1201	5.80
160°C	$C = 6.35e^{-2.0747t}$	0.9978	2.0747	0.33

C: Concentration (mg kg $^{-1}$) of carbary residues.

to their different physical and chemical prosperities. The significant decrease of carbofuran and carbaryl residues in primary made tea could be also due to the thermal decomposition of the tea leaves during processing.

Dissipation in tea roasting processing

For tea roasting, Tables 3 and 4 list carbofuran and carbaryl degradation flows in first order kinetics. Roasting temperature can be seen to play a significant role in reducing the pesticide residues. With higher roasting temperatures of 130°C and 160°C, the half-life of cabofuran were 7.20 and 0.57 hours, respectively. On the other hand, the half-life of carbaryl were 5.80 and 0.33 hours, respectively. The degradation rates obtained by varying roasting time between 1 and 6 hours for different temperature treatments are shown in Figure 3. In primary made tea, the initial residue deposits of carbofuran and carbaryl were 1.13 and 6.34 mg kg^{-1}, respectively. There was no significant change of carbofuran and carbaryl at 70°C for roasting times from 1 to 6 hours.

Comparing carbofuran and carbaryl residues in primary made tea after time roasting at 70°C, 100°C, 130°C and 160°C, there were no significant differences found between carbofuran and carbaryl at 70°C and 100°C. But at the high temperatures (130°C and 160°C) there was the greatest reduction of carbofuran and carbaryl (Fig. 3). For the primary made tea with roasting temperatures of 100°C to 160°C, there were significant decreases of carbofuran concentrations at first hour of roasting, residues were 1.03 and 0.35 mg kg^{-1}, respectively. And the carbaryl residue significantly decreased after the first hour of roasting under temperatures of 130°C and 160°C, the residues were 4.21 and 0.94 mg kg^{-1}, respectively. It is notable, that at higher roasting temperature (160°C), with 2 or more hours roasting, no measurable carbofuran and carbaryl residues were found. Similar results have been obtained by other authors for a variety of pesticides. For example, increased temperature during the cooking process has been shown to decrease pesticide residues.[19–20,23–24] Our results show that efficiency of the higher roasting temperature process yielded almost complete elimination of incurred residues of the carbofuran and carbaryl residues. The general trend was that as roasting temperature and time increased, the carbofuran and carbaryl residues decreased (Fig. 3). The present results suggest that carbofuran and carbaryl are heat-degradable, and roasting temperature at higher temperature can accelerate the breakdown of the pesticides molecules.

Conclusion

The present studies clearly show that in the field tea leaves sprayed with carbofuran or carbaryl at recommended dosages and at normal harvesting interval of 21 days after spraying are safe. Following Oolong tea manufacturing the carbofuran or carbary residues in primary-made tea decreased. Tea roasting at the higher temperatures greatly reduced carbofuran and carbaryl residues. It may be concluded that at the present recommend dosages of carbofuran and carbaryl application, and with a normal interval to harvesting and suitable manufacture processes including roasting, Oolong tea is safe for consumers.

Acknowledgments

We wish to thank the Council of Agriculture (Taiwan) for financing this project. The authors also wish to thank Yu Chu Liang, Hsiu Jung Hsieh, Pao Hua Chen, Li Hua Lin, Li Chen Lin, Su Chuan Hsieh, Zhen Wei Lin, Song Hui Chen and Zen Chang Chen for their skillful technical assistance.

References

[1] Nagayama, T.; Kobayashi, M.; Shioda, H.; Tamura, Y. Pesticide residues in imported raw agricultural commodity. J. Food Hyg. **1995**, *36*, 643–655.

[2] Neidert, E.; Saschenbreker, P.W. Occurrence of pesticide residues in selected agricultural food commodities available in Canada. J. Assoc. Off. Anal. Chem. **1996**, *79*, 549–566.

[3] Singh, R.P.; Agnihotri, N.P. Residues of dicofol, endosulfan, and malathion on tea *Camellia* sinesis L. J. Entomol. Res. **1984**, *8*, 14–16.

[4] Shivani, J.; Sood, C.; Kumar, V.; Ravindranath, S.D.; Shanker, A. Leaching of pesticides in tea brew. J. Agric. Food Chem. **2001**, *49*, 5479–83.

[5] Tzeng, D.D. The maximum residues levels in main export countries for Taiwan agriculture products. Tzeng, D.D. Eds. Agriculture and Food Agency. Nantou, Taiwan, **2005**, 275–287.

[6] Hsiao, S.N. Special crops insects and disease. In *Plant protection manual*; Fei, W.J., Wan, M.Y., Eds; Taiwan Agricultural Chemicals and Toxic Substances Research Institute: Taichung, Taiwan, **2004**, 569–599.

[7] Brahmaprakash, G.P.; Sethunathan, N. Metabolism of carbaryl and carbofuran in soil planted to rice. Agric. Ecosys. Environ. **1985**, *13*, 33–42.

[8] Deuel, L.E. Jr.; Brown, K.W.; Price, J.D.; Turner, F.T. Dissipation of carbaryl and the 1-naphthol metabolite in flooded rice fields. J. Environ. Qual. **1985**, *14*, 349–354.

[9] Campbell, S.; David, M.D.; Woodward, L.A.; Li, Q.X. Persistence of carbofuran in marine sand and water. Chemosphere **2004**, *54*, 1155–1161.

[10] Barba, A.; Carcia, S.N.; Camara, M.A. Disappearance of carbosulfan residues in peaches. Pestic. Sci. **1995**, *43*, 317–320.

[11] Zweig, G.; Gao, R.; Witt, J.M.; Popendorf, W.; Bogen, K. Dermal exposure to carbaryl by strawberry harvesters. J. Agric. Food Chem. **1984**, *32*, 1232–1236.

[12] Blazquez, C.H.; Vidyarthi, A.D.; Sheehan, T.D.; Bennett, M.J.; McGrew, G.T. Effect of pinolene (b-pinene polymer) on carbaryl foliar residues. J. Agric. Food Chem. **1970**, *18*, 681–684.

[13] Archer, T.E.; Stokes, J.D.; Bringhurst, R.S. Fate of carbofuran and its metabolites on strawberries in the environment. J. Agric. Food Chem. **1977**, *25*, 536–541.

[14] Bisen, J.S.; Ghosh, H.N. Persistence and degradation of some insecticides in Darjeeling tea. J. Plant. Crop **2000**, *28*, 123–31.

[15] Athanasopoulos, N.; Kyriakidis, V.; Panagiotis, S. A study on the environmental degradation of pesticides Azinphos Methyl and Parathion Methyl Panagiotis E. J. Environ. Sci. Health Part B **2004**, *39*, 297–309.

[16] Guillebeau, L.P.; All, J.N.; Javid, A.M. Influence of pyrethroid insecticides on boll weevil and bollworm in cotton. J. Econ. Entomol. **1989**, *82*, 291–297.

[17] Geisman, J.R. Reduction of pesticide residues in food crops by processing. Residue Rev. **1975**, *54*, 43–54.

[18] Elkins, E.R. Effect of commercial processing on pesticide residues in selected fruits and vegetables. J. Assoc. Off. Anal. Chem. **1989**, *72*, 533–535.

[19] Lee, S.R.; Mourer, C.R.; Shibamoto, T. Analysis before and after cooking processes of trace chlorpyrifos spiked in polished rice. J. Agric. Food Chem. **1991**, *39*, 906–908.

[20] Cabras, P.; Angioni, A.; Garau, V.L.; Menelli, E.V.; Cabitza, F.; Pala, M. Pesticide residue in raisin processing. J. Agric. Food Chem. **1998**, *46*, 2309–2311.

[21] Chen, Z.M.; Wan, H.B. Factors affecting residues of pesticides in tea. Pestic. Sci. **1998**, *23*, 109–118.

[22] Chitra, S.; Shivani, J.; Vipin, K.; Ravindranath, S.D.; Adarsh, S. How manufacturing processes affect the level of pesticide residues in tea. J. Sci. Food Agric. **2004**, *84*, 2123–2127.

[23] Ishikura, S.; Onodera, S.; Sumiyashiki, S.; Kasahara, T.; Akayama, M.; Watanabe, S. Evaporation and thermal decomposition of organophosphorus pesticides during cooking of rice. J. Food Hyg. **1984**, *25*, 203–208.

[24] Coulibaly, K.; Smith, J.S. Thermostability of organophosphate pesticides and some of their major metabolites in water and beef muscle. J. Agric. Food Chem. **1993**, *41*, 1719–1723.