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Dynamics of Carbendazim Residue in *Panax notoginseng* and Soil

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Abstract To provide scientific information for GAP of *P. notoginseng* and guiding the farmers and enterprises of Chinese medicine, dynamics of carbendazim residue in the Chinese medicinal herb, *P. notoginseng* and cultivated soil was studied at Wenshan County in 2008. The half lives of carbendazim in *P. notoginseng* were 5.92–6.82 day (soil), 6.71–6.77 day (fresh leaf), 3.29–3.93 day (fresh root), and 31.50–36.67 day (powder of the dry root) separately. Carbendazim residues in *P. notoginseng* were more stable during storage stage than growing stage.

Keywords Pesticide degradation · Carbendazim · *Panax notoginseng* · Redix Et Rhizoma Notoginseng · Chinese medicinal herb

Chinese medicinal herbs are used by more than 4 billion people all over the world. Radix Et Rhizoma Notoginseng is the dried root of *Panax notoginseng* (Burk.) F. H. Chen (Fam. Araliaceae), which is a most well-known traditional Chinese medicine. This medicinal herb is distributed throughout the southwest of China, Burma (Myanmar) and Nepal (Zhou et al. 1975). Radix Et Rhizoma Notoginseng is very effective for hematemesis, epistaxis, abnormal uterine bleeding, traumatic bleeding, and cardio-cerebrovascular diseases, and has also been regarded as a useful healthy protective ingredient (Han and Hu 1996; Ma et al. 1998; White et al. 2001). It has been used as a curative and protective ingredient in oriental traditional medicine for nearly 1,000 years, and the use of this herb is increasing. Currently Redix Et Rhizoma Notoginseng grows primarily (over 85%) in Wenshan county of China. The total production is about 10 million kg per year in China. Many products have been exported to Japan, Corea, Southeast Asia, Europe, and America. Commercial planting of *P. notoginseng* are affected by fungus diseases, and pesticides may be applied during growing stage to protect plants from plant diseases and insect damage (Feng et al. 2003; Han 2005).

Carbendazim, methyl-1H-benzimidazol-2-yl carbamate, is a widely used systemic fungicide on *P. notoginseng*. It is also a metabolic product of some other fungicides, such as benomyl and thiophanate-methyl (Anastassiades and Schwack 1998; Burrows and Edwards 2004), and published information on its chemical toxicity to human are numerous (Cuppen et al. 2000; Akbarsha et al. 2001; Nakai and Hess 1997). There are reports on the residual dynamics of carbendazim in soil (Jin et al. 2005; Xiang et al. 2008; Nannipieri and Bollag 1991; Tian et al. 2006; Zhang et al. 2006; Wei et al. 2009), but residual dynamics of carbendazim in *P. notoginseng* has not been reported. The objectives of the research reported here were to determine the fate of carbendazim in *P. notoginseng* and cultivated soil, and to provide

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information for safe application of this fungicide on cultivated *P. notoginseng*.

Materials and Methods

Analytical grade carbendazim (purity greater than 99%) was provided by China Standard Technology Development Corporation, Beijing, China; 50% WP carbendazim was provided by Sichuan Guoguang Agrochemical Co.(Ziyang, Sichuan, China). Other solvents or chemicals used in this study were analytical or HPLC-grade. Plants and cultivated soil were collected from *P. notoginseng* Test Station in Wenshan County, Yunnan Province, China, from September 23 to November 7, 2008. The physical and chemical properties of the soils were showed in Table 1.

Trial and control plots were 30 m^2 and protective lines were set up between trial plots. For the control of fungal diseases, 0.675 kg ai/ha (4.05 g 50% WP carbendazim to 1.5 L water) or 1.000 kg ai/ha (6.00 g 50% WP carbendazim to 1.5 L water) carbendazim was set and respectively sprayed in relative trial plots two times in 45 and 30 days before the harvest. Samples of soil, leaf and root of plants were collected at 2 h, 1, 3, 7, 12, 20, and 30 days after the second carbendazim application for determination of carbendazim residue. Every treatment was repeated three times.

Samples of fresh roots were dried in the oven at 49°C and pulverized. The powder was stored in the incubator at 5 and 20°C, respectively. The sample was collected after 2 h, 1, 3, 7, 15, 30 and 45 days for determination of carbendazim residue.

Samples of fresh roots of *P. notoginseng* were randomly collected from different farm fields at harvest (Table 4). A portion of the samples were dried in the oven at 49°C and pulverized for determination of carbendazim residue.

The analytical method of carbendazim residue referred to Jin et al. (2005). A HPLC–MS was also used to ensure a good selectivity, specificity, and accuracy. HPLC–MS was performed on a Waters Acquity Qquattro Premier Xe with an ACQUITY UPLC RP18 1.7 um 2.1 × 100 mm. The HPLC was performed with methanol + H_2O (1: 1, v/v) in a flow rate of 0.2 ml/min for 5 min. Mass spectrometer conditions were: ionization mode: ESI; mode: positive mode; voltage: capillary 3.00 kV; cone 40 v; extractor 3 v; RF lens 0; temperatures: source temp 120°C; desolvation temp 350°C; gas flow: desolvation 500 L/h; cone 50 L/h; mass scan range: 100–500 AMU, solvent delay 5.0 min.

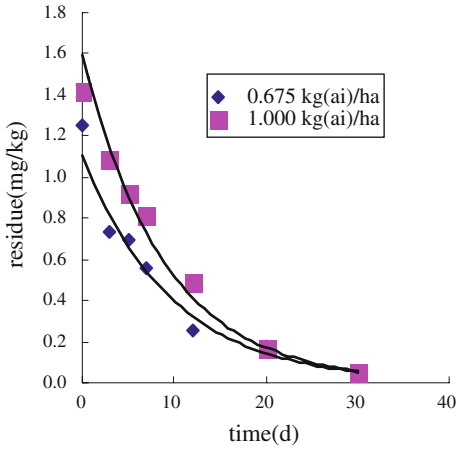

Fig. 1 Dissipation curve of carbendazim in soil

The minimum detectable concentration of HPLC method is 0.005 mg/kg, and the average recoveries of carbendazim at 0.05–5.00 mg/kg fortified level in *P. notoginseng* and soil were 86.0%–96.2%, with RSDs of less than 9.6%.

Results and Discussion

The dissipation curve of carbendazim in the cultivated soil is shown in Fig. 1. The initial concentrations of carbendazim detected in soil were 1.250 mg/kg (0.675 kg ai/ha) and 1.421 mg/kg (1.000 kg ai/ha) separately 2 h after carbendazim sprayed, and the dissipation dynamics followed the first order kinetics. The half lives of carbendazim were 5.92 day (SD = 0.08 day, 1.000 kg ai/ha) and 6.82 day (SD = 0.16 day, 0.675 kg ai/ha) separately in the cultivated soil (Table 2), and the carbendazim 1.000 kg ai/ha disappeared more quickly than that 0.675 kg ai/ha. The difference was significant ($p < 0.05$). The behavior of carbendazim in Radix Ophiopogonis soil was similar. The half lives were 7.07 day (0.675 kg ai/ha) and 5.75 day (1.000 kg ai/ha)(Wei et al. 2009). Xiang et al. (2008) reported that half lives of carbendazim in soil were 8.6 day (2.0 mg/kg) and 6.8 day (4.0 mg/kg) in laboratory simulation, respectively. Nannipieri and Bollag (1991) reported

Table 1 Physical and chemical properties of soils used in the study

Soil types	pH	OM %	>0.25 (mm)	0.25–0.05 (mm)	0.05–0.01 (mm)	0.01–0.005 (mm)	0.0005–0.0001 (mm)	Physical clay (>0.01) %	Physical sand (>0.01) %
Loamy clay	5.28	2.78	0.676	7.04	49.5	20.2	14.1	42.8	57.2

Table 2 Dynamics of carbendazim residue in *P. notoginseng* and soil

Part	Sprayed concentration (kg ai/ha)	Degradation equation	Correlation coefficient r	Half-life $\bar{x} \pm$ SD (d)
Soil	0.675	$y = 1.1063e^{-0.1017x}$	0.9919	6.82 ± 0.16
	1.000	$y = 1.5983e^{-0.1117x}$	0.9966	5.92 ± 0.08
Fresh leaf	0.675	$y = 153.59e^{-0.1024x}$	0.9782	6.77 ± 0.23
	1.000	$y = 222.54e^{-0.1033x}$	0.9841	6.71 ± 0.07
Fresh root	0.675	$y = 1.0975e^{-0.2122x}$	0.9889	3.93 ± 0.11
	1.000	$y = 1.4491e^{-0.1763x}$	0.9537	3.29 ± 0.03

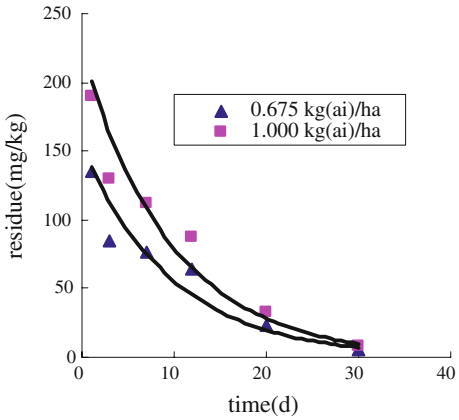

Fig. 2 Degradation curve of carbendazim in leaf

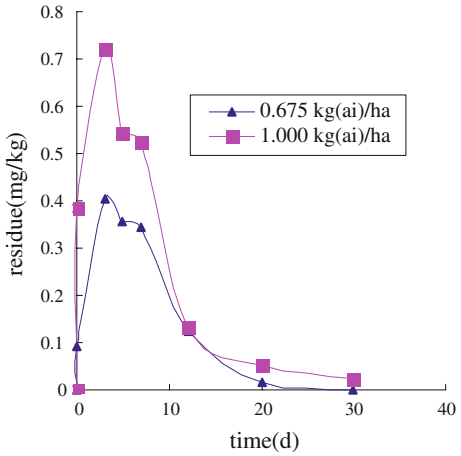

Fig. 3 Residue dynamic curve of carbendazim in fresh root

that the soil microorganism preferred other carbon source compounds to the pesticide when the pesticide residues were fewer, therefore the carbendazim of lower concentration dissipated more slowly than that of higher concentration. There were other reports on the half lives of carbendazim in soil that ranged from 3.63 to 57.1 day (Jin et al. 2005; Tian et al. 2006; Zhang et al. 2006). The remarkable difference indicated that the plants and environment factors, especially the soil type, would greatly influence the soil half life of carbendazim.

The degradation curve of carbendazim in leaves is shown in Fig. 2. The residue dynamics followed the first order kinetics. The half lives of carbendazim were 6.71 day (SD = 0.07 day, 1.000 kg ai/ha) and 6.77 day (SD = 0.23 day, 0.675 kg ai/ha) in leaves (Table 2). The statistical results indicated that there was no remarkable difference in half lives of two test concentrations in leaves of *P. notoginseng* ($p > 0.05$).

The dynamic curve of carbendazim residue in fresh roots is presented in Fig. 3. The initial concentrations were very low, but residues increased quickly during the first few days, and peaked on the third day then decreased. The half lives of carbendazim were 3.29 day (SD = 0.03 day, 1.000 kg ai/ha) and 3.93 day (SD = 0.11 day, 0.675 kg ai/ha) separately in the fresh roots (Table 2). Carbendazim acts a systematic fungicide, and although it was mainly sprayed on leaves of the plant, it may be conducted from leaf to root. The root also might absorb the pesticide from the soil. During the first 3 days the conduction and adsorption may be stronger than the degradation in the root and the carbendazim accumulated quickly; it reached a maximum on the third day. With the concentration increasing, degradation speed of carbendazim exceeds accumulation in the root, and the residue started decreasing. The similar behavior of carbendazim in ginseng and Radix Ophiopogonis were reported (Tian et al. 2006; Wei et al. 2009).

The degradation curve of carbendazim in the powder of dry root is presented in Fig. 4. The degradation dynamics followed the first order kinetics (Table 3). Carbendazim residues degraded slowly compared to fresh root, and the half lives of carbendazim residue in dry root powder were 31.50 day (SD = 2.92 day) at 20°C and 36.67 day (SD = 4.07 day) at 5°C separately. Degradation followed the rule that the higher the temperature the quicker a pesticide degrades, but the degradation speed only increased 16.4% from 5 to 20°C.

The final residues of carbendazim in dry and fresh roots of *P. notoginseng* were shown in the Table 4. Carbendazim residues in dry root were nearly two times of those in fresh roots. As the water content of fresh roots was 46.2–53.7%,

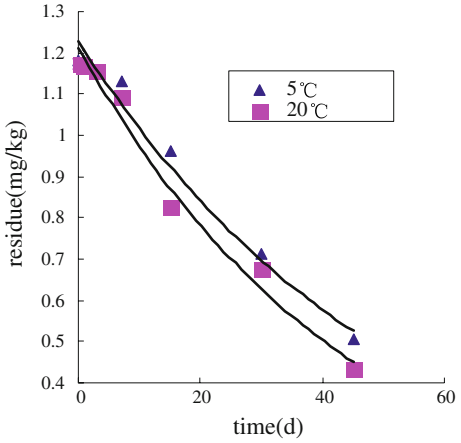

Fig. 4 Degradation curve of carbendazim in powder of dry root

Table 3 Dynamics of carbendazim in dry root powder of *P. notoginseng*

Temperature (°C)	Degradation equation	Correlation coefficient *r*	Half-life $\bar{x} \pm$ SD (*d*)
5	$y = 1.2282e^{-0.0189x}$	0.9935	36.67 ± 4.07
20	$y = 1.213e^{-0.0220x}$	0.9920	31.50 ± 2.92

Table 4 Final residues of carbendazim in dry and fresh roots of *P. notoginseng*

Place	Carbendazim residues $\bar{x} \pm$ SD (mg/kg)	
	Dry root powder	Fresh roots
Fatulong village in Jiansan County	0.402 ± 0.023	0.226 ± 0.018
Wuai village in Wenshan County	1.159 ± 0.074	0.651 ± 0.044
Hezhan village in Wenshan County	0.947 ± 0.032	0.517 ± 0.027
Aolongke Test Station in Wenshan County (1.000 kg ai/ha)	0.042 ± 0.009	0.026 ± 0.007
Aolongke Test Station in Wenshan County (0.675 kg ai/ha)	ND	ND

ND means that the residue was below 0.005 mg/kg

it indicated that the process of dryness had little effect on the degradation of carbendazim residues. There were great differences of carbendazim residues from place to place comparing the results. Carbendazim residues in both Wuai and Hezhan were higher than that in Fatulong or Aolongke, which indicated that the carbendazim might be still sprayed by farmers near the harvest.

The half lives of carbendazim in *P. notoginseng* were 5.92 day (1.000 kg ai/ha, soil), 6.82 day (0.675 kg ai/ha, soil), 6.77 day (0.675 kg ai/ha, fresh leaf), 6.71 day (1.000 kg ai/ha, fresh leaf), 3.29 day (1.000 kg ai/ha, fresh root), 3.93 day (0.675 kg ai/ha, fresh root), and 31.50 day (1.000 kg ai/ha, dry root powder) and 36.67 day (0.675 kg ai/ha, dry root powder) separately. The result indicated that Carbendazim residues in *P. notoginseng* were more stable during storage stage than growing stage.

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