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Degradation of Imidacloprid in Chrysanthemi Flos and Soil

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Abstract Degradation of imidacloprid in chrysanthemi flos and cultivated soil was studied. The half-lives of imidacloprid were 3.55–5.17 days (soil), 2.10–3.98 days (fresh buds and flowers), 22.14 days (dry flowers, 5°C) and 13.08 days (dry flower, 20°C), separately. The temperature can affect imidacloprid degradation in soil and dry chrysanthemum buds and flowers. Imidacloprid residues in chrysanthemum flowers were more stable during store stage than growing one. Few imidacloprid residues would be dissolved into chrysanthemum tea liquor when the residue in dry buds or dry flowers was below 0.8 mg/kg.

Keywords Pesticide degradation · Imidacloprid · Chrysanthemi flos

Chrysanthemum flower is the disk florets of *chrysanthemum morifolium* Ramat. It can be made into food, beverage and medicine. In medicinal uses, extracts of chrysanthemum plants (stem and flower) have been shown to have a wide variety of potential medicinal properties, including anti-HIV-1(Collins et al. 1997; Hu et al. 1994), antibacterial(Sassi et al. 2008) and antimycotic(Marongiu et al. 2009). Because the chrysanthemum is a cultivated plant and often attacked by aphids and larvae of some Lepidoptera species. It is very popular to spray insecticides to control the damage of these pests in chrysanthemum fields.

Imidacloprid [IUPAC name 1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylideneamine] is an insecticide that is popularly used in chrysanthemum fields. In order to control the residue of imidacloprid in chrysanthemum buds and flowers, it is necessary to realize the behavior of imidacloprid in chrysanthemum buds, flowers and cultivated soil. By now, there are some reports on degradation of imidacloprid in soil, fruits, vegetable and other crops (Ju et al. 2006; Lou et al. 2004; Guan et al. 2010; Rouchaud et al. 1994; Miles Inc 1993; Scholz and Spiteller 1992; Baskaran et al. 1999; Kousik Mandal et al. 2010; Thai et al. 2009; Sherif et al. 2008; Ayman et al. 2007; Parshotam et al. 2009; Sanyal et al. 2006). However, no any report about residue and degradation of imidacloprid in chrysanthemum buds, flowers and their cultivated soil were found. The object of current research is to study the residue and degradation of imidacloprid in chrysanthemum bud, flower and cultivated soil, and provide scientific data for formulating the safety interval of imidacloprid in chrysanthemum buds and flowers.

Materials and Methods

Imidacloprid of analytical grade was brought from China Standard Technology Development Corporation (Beijing, China). The LC-grade water was provided by Institute of Agrochemistry, Zhejiang University (Hangzhou, China), and both the water and the methanol of HPLC grade used in liquid chromatography were passed through a 0.45 pm filter before use. Other solvents or chemicals used in this study were of analytical or HPLC grade. Chrysanthemum

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buds, flowers and their cultivated soil were collected at Tongxiang city where chrysanthemum genuine regional planting area, Zhejiang province, China. The trial soil was loamy clay. The pH, OM and physical clay were 7.41, 1.09 and 42.8%.

Every trial plot was about 30 m^2. Trials and control plots were randomly selected and the protective lines were set up between trial plots. Every treatment was replicated three times. According to the starting damage time of aphid and noctuid, 40 g ai/ha was sprayed in trial plots on Sep. 18, 2008, 2009. Then 40 and 60 g ai/ha imidacloprid were separately sprayed in trial plots on different day before the harvest. Samples of cultivated soil and fresh buds and flowers of chrysanthemum were randomly collected at same harvest day for detecting.

Twenty-Four of 250 mL flasks were selected as one group. Every flask was added 50 g test soil (a kind of typical chrysanthemum cultivated soil located in Tongxiang, Zhejiang province, China) that grinded and passed through 20 mesh screen. The soil water content was remained at 60% field water content. Every group was fortified 1 mL of 50 mg/L imidacloprid prepared solution, separately. Every flask was covered with a cap, mixed and stored in 10, 20 and 30°C culture chambers for analysis at different intervals. The sample of dry flowers which contain suitable imidacloprid residue was selected and put in a 5 or 20°C culture chamber, separately. Suitable amount of sample was taken for analysis at different intervals.

Twenty gram of soil was weighed and put into a 250 mL bottle with screw cap. 70 mL dichloromethane, 1 mL (1 mol/L) hydrochloric acid and 1 g Celite545 were added. The cap of bottle was screwed and extracted for 30 min under ultrasonic. The extracted solution was filtrated through Bucher that covered with a thin layer of Celite545 into a 250 mL of flask. The residue was washed with 30 mL dichloromethane, dehydrated with anhydrous sodium sulfate, collected the solution and concentrated to about 1 mL by a rotary vacuum evaporator at 30°C. Then the extracted solution was blown to dry with nitrogen. Five milliliter methanol was added, transported to a centrifuge tube and centrifuged for 5 min at 3,000/min. Three milliliter solution was passed through a 0.45 μm filter film for HPLC detecting.

Fresh buds or flowers were cut with scissors. 10 g samples were weighed into a 250 mL bottle with screw cap. 100 mL methanol–water (7: 3, v/v), 1 mL (1 mol/L) hydrochloric acid and 1 g Celite545 was added. The cap of bottle was screwed and extracted for 30 min under ultrasonic. The extracted solution was filtrated through Bucher that covered with a thin layer of Celite545 into a 250 mL of flask. The residue was washed with 30 mL of dichloromethane and the filtrate was collected into a 250 mL separating funnel, extracted with 40, 40, 30 mL dichloromethane and dehydrate with anhydrous sodium sulfate. Collected the extracted solution and concentrated to about 1 mL by a rotary vacuum evaporator at 30°C for clean up.

The concentrated extracts were put on a glass column (25 × 2.0 cm, the bottom carrying sand core, with a 30 mL reservoir, adding 2 cm anhydrous sodium, mixtures of 7.0 g Florisil and 5.0 g neutral alumina, 2 cm anhydrous sodium from the top down, pre-eluted the column with 30 mL petroleum ether), eluted with 40 mL petroleum ether-ethyl acetate (95:5 v/v), discard the eluate and eluted with 50 mL acetonitrile again, collected the eluate and evaporated to 1 mL with a rotary vacuum evaporate at 60°C, evaporated to dry with nitrogen. Adjusted the volume to 5 mL with methanol and passed through a 0.45 μm filter film for HPLC detecting.

The dry buds or dry flowers were grinded and passed through a 20 mesh screen. 5.0 g sample was weighed into a 250 mL bottle with screw cap. Next step same as fresh flower method.

One gram of dry buds or dry flowers of chrysanthemum was weighed into a 250 mL bottle with screw cap. First extraction: 100 mL of pure water (85°C) was added and stood for 20 min. The tea liquor was filtered into a 250 mL separating funnel, extracted with 60, 40, 30 mL dichloromethane and dehydrated with anhydrous sodium sulfate. Next step same as fresh flower method. Second extraction: After first extracting of the flower residue, 100 mL of pure water (85°C) was added and stood for 20 min. The tea liquor was filtered into a 250 mL separating funnel, extracted with 60, 40, 30 mL dichloromethane again and dehydrated with anhydrous sodium sulfate. Next step same as fresh flower method.

HPLC determination. Column: Diamonsil (TM) C_{18}, 5 μm, 250 × 4.6 μm; mobile phase:methanol:acetonitril: water = 20:20:60; flow rate: 1 mL/min; detecting wavelength: 270 nm; injecting volume: 10 μL.

Results and Discussion

The method has demonstrated acceptable performance for the imidacloprid residue analysis. The detector response was linear in the range of 0.05–10 ng. The LOQ of imidacloprid for dry flower, fresh flower and soil samples was 0.01 mg/kg separately. Average recoveries of imidacloprid in soil, fresh flower, dry flower and tea of chrysanthemum fortified from 0.05 to 2.0 mg/kg were 88.80–98.33% (soil), 84.60–96.24% (fresh flower), 86.12–96.51% (dry flower) and 84.60–93.07% (chrysanthemum tea liquor).

The persistence of imidacloprid in soil was studied at 10, 20 and 30°C three temperature levels. The results indicated that the degradation of imidacloprid at different temperature was followed the first order kinetics. The degradation curves were shown in Fig. 1. The half lives of

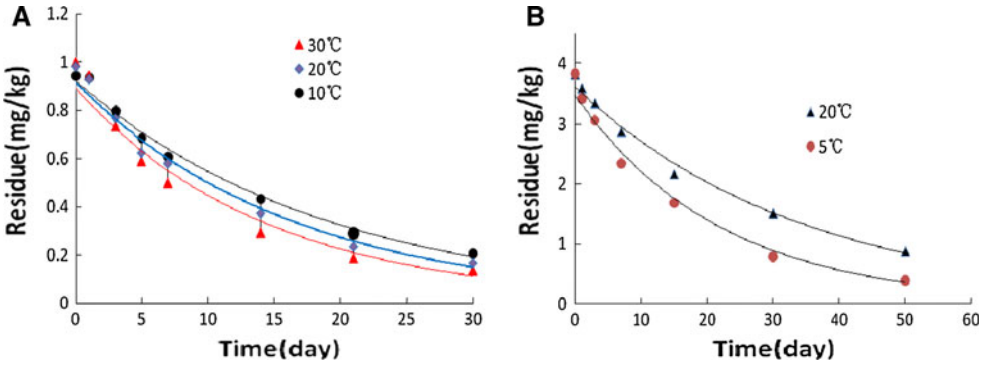

Fig. 1 Degradation curves of imidacloprid in dry flowers of chrysanthemum and soil at different temperature (**a** is soil; **b** is dry flowers)

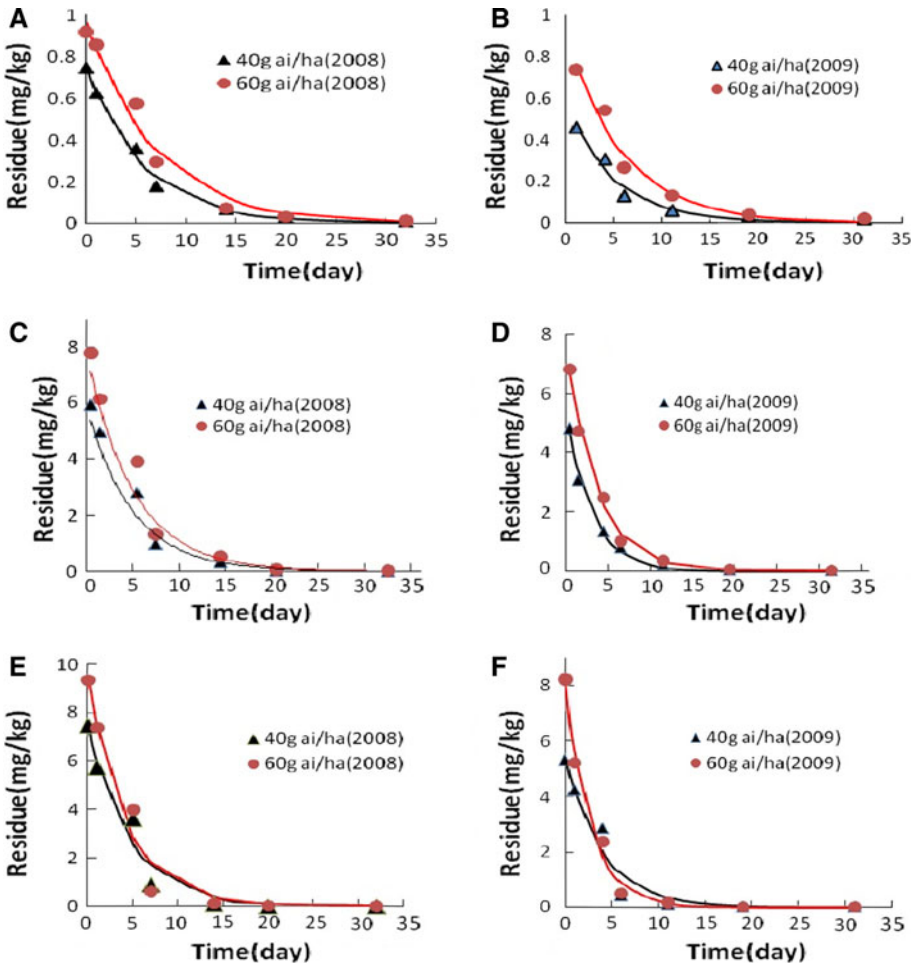

Fig. 2 Dissipation curve of imidacloprid in chrysanthemum and soil (**a** and **b** is soil; **c** and **d** is fresh bud; **e** and **f** is fresh flower)

imidacloprid in soil were 12.27 days (10°C), 10.00 days (20°C) and 7.85 days (30°C) under laboratory condition. There was no remarkable difference of half lives between 10 and 20°C after static analysis. This indicated that it can obviously affect degradation of imidacloprid when temperature increases to more high level.

The dissipation curves of imidacloprid in the field soil were shown in Fig. 2. The dissipation dynamics followed the first order kinetics. The half lives of imidacloprid were 3.55 days (40 g ai/ha, 2008), 4.86 days (60 g ai/ha, 2008), 4.47 (40 g ai/ha, 2009) and 5.17 days (60 g ai/ha, 2009) in the field soil, separately, and two test concentration no remarkable difference. The result showed that half life of imidacloprid in field soil was short and similar with tea garden soil (Ju et al. 2006), cabbage soil (Lou et al. 2004) and soybean soil (Guan et al. 2010).

Comparing to room and field test results, the half lives of room test were 2–3 times of field test. Faster imidacloprid loss in the field soil possibly resulted from the low Koc of 132–310 and a high water solubility of 514 ppm,

Table 1 Imidacloprid residue in chrysanthemum tea liquor

Dry dud			Dry flower		
Pesticide Residue (mg/kg)	First extract (%)	Second extract (%)	Residue (mg/kg)	First extract (%)	Second extract (%)
10.195 ± 0.116	30.20 ± 2.83	3.85 ± 0.39	14.530 ± 0.160	12.99 ± 0.94	0.39 ± 0.06
9.101 ± 0.178	16.04 ± 1.15	2.60 ± 0.47	10.647 ± 0.246	11.90 ± 0.42	ND
1.824 ± 0.017	43.15 ± 6.36	ND	3.512 ± 0.023	10.62 ± 0.92	ND
0.859 ± 0.033	7.57 ± 1.51	ND	1.138 ± 0.042	17.75 ± 2.37	ND
0.116 ± 0.013	ND		0.219 ± 0.020	ND	

although earlier field studies, under normal weather conditions, had found imidacloprid to be relatively immobile in silt loam soils (Rouchaud et al. 1994). The moderate Kow value of 3.7, combined with its rapid photo degradation in water (half-life ($t_{1/2}$) < 3 h) and on soil ($t_{1/2}$ 39 days), suggested a low potential for bioaccumulation.

The dissipation curves of imidacloprid in fresh buds and flowers of chrysanthemum were shown in Fig. 2. The dissipation dynamics followed the first order kinetics. The half lives of imidacloprid in fresh buds and flowers in 2008 and 2009 were 3.44–3.98 days (40 g ai/ha, bud), 3.48–3.92 days (60 g ai/ha, bud), 2.21 days (40 g ai/ha, flower) and 2.10–2.19 days (60 g ai/ha, flower), separately, and two test concentrations no remarkable difference in 2 year tests. But there was remarkable difference between buds and flowers in half lives of imidacloprid ($p < 0.05$). Dissipation of imidacloprid in flowers was quicker than in buds. The completely abloom flower has greater surface area than bud. It probably makes imidacloprid exposure under much more sunlight, rainfall and other environmental condition that causes degradation and dissipation of imidacloprid.

The persistence of imidacloprid in dry flowers was studied at 5 and 20°C temperature levels in culture chamber. The results (Fig. 1) indicated that the degradation of imidacloprid at different temperature was followed the first order kinetics. The half lives were 22.14 days (5°C) and 13.08 days (20°C). There was remarkable difference of half lives between 5 and 20°C after static analysis ($p < 0.01$). This indicated that it can obviously affect degradation of imidacloprid when temperature increases to more high level. Comparing the result of field flower test, it proves that imidacloprid in dry chrysanthemum products is more persistent during storage.

The result of imidacloprid residue in chrysanthemum tea liquor was shown in Table 1. It indicated that the residue in buds was easier into tea liquor than flowers, and there was more imidacloprid residue in chrysanthemum tea liquor first made. Sanyal et al. (2006) reported that imidacloprid was rapidly dissipated in processed tea following first order reaction kinetics at all application rates and had half-lives of 0.91–1.16 days with the residue in tea liquor found to be below detectable limit on 3rd day sample(Sanyal et al. 2006). It is similar to our test results, only very few imidacloprid residues would be dissolved in chrysanthemum tea liquor when it was below 0.8 mg/kg in dry buds and flowers. Usually, it will concentrate five times when fresh flowers of chrysanthemum were processed into dry one. According to the test, the residue of imidacloprid in dry buds and flowers will be below detectable limit when the residue in fresh buds and flowers was below 0.05 mg/kg and after they were processed into dry one. Therefore, it is safe for human health if 0.05 mg/kg is recommended as maximum residue limit of imidacloprid for fresh chrysanthemum buds and flowers, and 20 days as safety pre-harvest interval.

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