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Environmental behaviors of phoxim with two formulations in bamboo forest under soil surface mulching

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ABSTRACT

Phoxim (emulsifiable concentrate (EC) and granules (G)) has been widely used in bamboo forests. The persistence and magnitude of phoxim residues in the crop and soil must be investigated to ensure human and environmental safety. The environmental behaviors of the two formulations were investigated in a bamboo forest under soil surface mulching conditions (CP) and non-covered cultivation conditions (NCP). The half-lives of phoxim in soil under the two conditions in soil were 4.1–6.2 days (EC) and 31.5–49.5 days (G), respectively. Phoxim in EC could be leached from the topsoil into the subsoil. A minimized leaching effect was observed for G under NCP. Inversely, an enhanced leaching effect was observed for G under CP. The G formulation resulted in more parent compound (in bamboo shoots) and metabolite (in soil) residues of phoxim than in the case of EC, especially under CP conditions. In addition, the intensity and duration of the formulation effect on soil pH adjustment from G were more obvious than that from EC. Results showed that the environmental behaviors (distribution, degradation, residue) of phoxim in the bamboo forest were significantly influenced by the type of formulation. The prolongation effect from phoxim G might cause persistence and long-term environmental risk. However, bamboo shoot consumption could be considered relatively safe after applying the recommended dose of the two phoxim formulations.

Introduction

Bamboo shoot is one of the most popular types of non-timber forest product in Asian countries, and China is the world's largest producer and exporter. The bamboo shoots are exported to the USA, EU and Japan in large quantities every year. Although various practices are conducted to minimize the damage caused by insects during bamboo growth, the most effective strategy is still the application of insecticides. Phoxim, an organophosphorus pesticide with relatively high efficiency and low toxicity, is frequently employed in soil and foliage. In China, phoxim is applied to control underground pests in bamboo forests and for other plants, with application of up to 1000 tons per year (Huang et al., 2013). The emulsifiable concentrate (EC) of phoxim has been commonly used for many years. However, excessive application of insecticides will lead to great risk to the environment and human health (Wang et al., 2012). The use of a controlled-release formulation (CRF) is one of the best strategies to reduce the consumption of insecticide, and minimize its negative impact on the environment. CRFs produce a gradual and controllable release of insecticide over time, which allows a lower concentration of active ingredients to act effectively. In recent years, granules (G) of phoxim have also been applied in bamboo forests, especially for soil surface mulching cultivation.

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During bamboo shoot production, soil surface mulching (bamboo leaf, straw and/or rice chaff are spread on the soil to increase the soil temperature and bring forward the harvest time about 1 month) emerged as an important industry practice in the 90s of the last century and has been becoming more and more popular. The food safety issue caused by contamination by pesticide residues arouses more concerns. Therefore, good knowledge of the pesticide fate in foodstuffs will benefit from properly assessing the human exposure and the environmental risk. However, the available studies on the environmental fate of phoxim are either too old to keep up with the times (Hohl and Barz, 1995; Mason and Meloan, 1976), or seldom focused on the influence of different formulations on its dissipation and residues in the field (Lin et al., 2011).

The different toxic effects induced by diverse pesticide formulations had been confirmed for bovine culture cells (Holeckova et al., 2013), microorganisms (Joly et al., 2013) and dermal exposure of pesticide operators (Berenstein et al., 2014). In addition, some previous works have focused on the influence of formulation on mobility (Wlodarczyk, 2014), leaching (Potter et al., 2010) and transport (Paradelo et al., 2014) of pesticides in soil under laboratory and field conditions. For example, the use of alginate CRF (alginate capsules) reduced the vertical mobility of metazachlor into the soil layer in comparison with the suspension concentrate (SC) formulation in soil column tests (Wlodarczyk, 2014). The influence of CRFs on pesticide loss by leaching has been studied using field-deployed lysimeters together with rainfall simulation (Potter et al., 2010); the authors reported that the use of a CRF with a clay-alginate polymer can decrease metolachor leaching. Furthermore, different pesticide formulations often result in the same active ingredients presenting different half-lives and terminal residues in plants and soil (Cao et al., 2005; Zhou et al., 2014). The degradation rate of chlorfenapyr nanoformulation was faster than that of SC, and the residue of the former was also less in soil (Cao et al., 2005). Many scientists concluded that the additives in the formulations were responsible for the differences (Paramasivam and Chandrasekaran, 2013; Sharma et al., 2011). In field and laboratory conditions, compared with the results from metazachlor applied alone, the addition of an adjuvant caused an increase of metazachlor residues at harvest time. Adjuvant addition caused a slowdown of leaching of metazachlor into the soil profile. Moreover, the addition of oil and surfactant adjuvants slowed down the degradation of metazachlor in soils (Kucharski and Sadowski, 2011).

However, few reports were taken into account the probable effects of different cultivation processes (field, greenhouse, soil surface mulching, *etc.*) on the effects of pesticide formulations. In recent years, some scientists found that the cultivation process had a notable effect on pesticide dissipation. For example, the dissipation rate of cyprodinil under greenhouse conditions was much faster than for field conditions, either in strawberries or in soil (Liu et al., 2011). The half-lives of chlorpyrifos in greenhouse cucumbers (Liang et al., 2012) and rice (field conditions) (Zhang et al., 2012) were 1.60 days and 4.28 days, respectively. In our previous work (Liu et al., 2014), the degradation and metabolism of chlorpyrifos in a bamboo forest under two conditions (with and without soil surface mulching) were investigated. Results indicated that the soil surface mulching had a notable effect on the degradation, leaching, metabolism of chlorpyrifos granules. To the best of our knowledge, there is no information available about the behaviors (degradation, distribution, residues) of phoxim in bamboo forests. In particular, the influence of EC and G formulations on phoxim behaviors under soil surface mulching is not yet clear. The objective of this study was to evaluate the effect of formulation on phoxim residues in a bamboo forest under soil surface mulching conditions, by comparing the phoxim dissipation rates and terminal residues between EC and G formulations. This data would be helpful for the establishment of Maximum Residue Levels (MRLs) for phoxim EC and G products. The present work was also designed to investigate the residues of the two phoxim formulations in bamboo shoots and soil so as to determine the acceptable interval between spraying and harvest, which would be beneficial to the safe use of this plant and the reduction of any consumer health risks.

1. Materials and methods

1.1. Reagents and solutions

Pesticide analytical standards were purchased from the National Information Center for Certified Reference Materials (Beijing, China), with certified quality. Individual pesticide stock solutions (100 mg/L) were prepared in methanol and stored at −20°C. Then, a series of dilutions containing the mixture of standards were prepared (10 mg/L) in methanol. HPLC-grade acetonitrile and methanol were obtained from Merck (Merck, Darmstadt, Germany). A Milli-Q-Plus ultrapure water system from Millipore (Milford, MA, USA) was used throughout the study to obtain HPLC-grade water for the analyses. Other solvents were from Shanghai Sanying Chemical Reagents (Shanghai, China), with pesticide residue analysis quality.

1.2. HPLC-MS/MS

The LC system consists of a high performance liquid chromatograph (Waters, Milford, MA, USA) with a HSS T3 column (5 μm, 100 mm × 2.1 mm, *i.e*., Waters). The mobile phase involving solvent A (0.05% formic acid, in water) and solvent B (acetonitrile) was eluted using a gradient program as follows: 80:20 of A:B (initial), 10%–90% A with 90%–10% B (0–5 min), 10:90 A:B (5–10 min), 10%–80% A with 90%–20% B (10–14 min),80:20 A:B (14–15 min). A subsequent re-equilibration time (3 min) was allowed between injections. The flow rate was 0.3 mL/min and the injection volume was 10 μL. The column and sample temperatures were maintained at 35°C.

MS/MS was performed on a Waters Quattro Premier triple-quadruple mass spectrometer equipped with an ESI source (Waters, Milford, MA, USA). MS/MS detection was performed in positive ion mode for phoxim and in positive mode for chlorphoxim separately. The monitoring conditions were optimized for the target compounds. Acquisition parameters were as follows: capillary voltage 3.5 kV, cone voltage 45 V, source block temperature 80°C, cone gas 50 L/hr, desolvation temperature 450°C, desolvation gas (nitrogen gas) 550 L/h, respectively. 298.9 (*m*/*z*) was selected as the precursor ion for phoxim, and its quantitative and qualitative