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Persistence and residual toxicity of two pirimiphos-methyl formulations on wheat against three stored-product pests

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ABSTRACT

The persistence and residual efficacy of two pirimiphos-methyl formulations [emulsifiable concentrate (EC) and capsule suspension (CS)] on wheat were evaluated in laboratory bioassays against adults of *Sitophilus granarius*, *Rhyzopertha dominica* and *Tribolium confusum*. Pirimiphos-methyl was applied at two doses, 2 and 4 mg kg^{-1}, on wheat and a bioassay was initiated at the day of application and every 4 weeks for 7 consecutive months (8 bioassays). In each bioassay, insect mortality was assessed after 7, 14 and 21 d of exposure, whereas after the final mortality count, all individuals were removed and progeny production was evaluated after an additional period of 65 d. Moreover, samples of the treated wheat were taken at the beginning of each bioassay to study the fate of pirimiphos-methyl during the storage period of 7 months by measuring insecticide residues by high performance liquid chromatography (HPLC). Both pirimiphos-methyl formulations provided long-term protection against *S. granarius* adults. In most cases, complete (100%) mortality was noted, while mortality exceeded 95% after 21 d of exposure even 7 months after application for both doses and formulations. *Tribolium confusum* mortality did not reach 100% for any of the combinations tested, while a gradual decline of mortality levels was recorded over the 7-month period of storage. *Rhyzopertha dominica* was the least susceptible species to pirimiphos-methyl with very low mortality levels already after 1 month of storage. The residue analysis results show that pirimiphos-methyl is persistent under the conditions tested, as more than 50% of the initial concentration was still present on the wheat grains after the 7-month period of storage, for both doses and formulations. From the residue analysis results CS was shown to be slightly more persistent than EC, however this was not expressed as a significantly higher insecticidal efficacy of CS over time compared to EC.

1. Introduction

Pirimiphos-methyl is a broad spectrum organophosphate insecticide, widely used as grain protectant globally (Redlinger et al., 1988). So far, pirimiphos-methyl has proved to be very effective against a wide range of stored-product insect pests (Huang and Subramanyam, 2005; Kljajić and Perić, 2007). Recently, Rumbos et al. (2013) investigated the efficacy of two pirimiphos-methyl formulations as grain protectants against seven stored-product insect species and reported high mortality rates for most of the species tested. Similarly, pirimiphos-methyl provided complete (100%) control of four psocid (Psocoptera) species on maize (Athanassiou et al., 2009). In another study, pirimiphos-methyl was effective against twelve populations of the granary weevil, *Sitophilus granarius* (L.) (Coleoptera: Curculionidae), causing mortality rates between 76 and 100% after 24 h of contact with treated filter paper (Kljajić and Perić, 2006). Nevertheless, there is still little information available on the long-term activity and the residual efficacy of pirimiphos-methyl against stored-product insects.

The capability of a grain protectant to provide long-term protection against stored-grain insects is one of the most desired characteristics, given that significant quantities of grains are stored

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for long periods, and are eventually processed right before the next harvest. Vayias et al. (2010) reported that spinosad could successfully provide protection for 6 months against the rice weevil, *Sitophilus oryzae* (L.) (Coleoptera: Curculionidae), and the lesser grain borer, *Rhyzopertha dominica* (F.) (Coleoptera: Bostrychidae), but not against the confused flour beetle, *Tribolium confusum* Jacquelin du Val (Coleoptera: Tenebrionidae) and the flat grain beetle, *Cryptolestes ferrugineus* (Stephens) (Coleoptera: Laemophloeidae). Similarly, three pyrethroid compounds, deltamethrin, alpha-cypermethrin and beta-cyfluthrin provided long term protection for more than 4 months in wheat against *S. oryzae* (Athanassiou et al., 2004a), whereas only beta-cyfluthrin provided a satisfactory level of protection against *T. confusum* adults six months post-application (Athanassiou et al., 2004b). Abo-Elghar et al. (2004) investigated the persistence and residual activity of an EC formulation of pirimiphos-methyl, applied at 25 mg kg^{-1}, against the cowpea weevil, *Callosobruchus maculatus* (F.) (Coleoptera: Bruchidae), for a period of 8 months and concluded that it could effectively reduce oviposition of *C. maculatus* throughout a storage period of 8 months post-application.

Insecticide persistence and dissipation patterns in the treated substrate is a matter of major current concern, as it relates with residual insecticidal efficacy, as well as with pesticide residues in the treated stored raw grains and the processed products. For instance, Fang et al. (2002) investigated the persistence and insecticidal activity of spinosad under field conditions over a period of 1 year and found that spinosad residues were stable and its efficacy was consistent against adults of *R. dominica* and the red flour beetle, *Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae), throughout the trial. For the same active ingredient, Chintzoglou et al. (2008) found that the dissipation of spinosad was higher on maize than on wheat, whereas the same was recently reported for indoxacarb for the lowest dose tested (Miliordos et al., 2017). For pirimiphos-methyl, a number of studies investigated its dissipation with time (Holland et al., 1994; Abo-Elghar et al., 2004; Balinova et al., 2006; Fleurat-Lessard et al., 2007), however, in most cases dissipation patterns were not correlated with its residual activity. Moreover, previous studies refer to older formulations (e.g. EC).

In the current study, we evaluated the insecticidal and residual effect of a newer type of pirimiphos-methyl formulation, known as capsule suspension (CS), against three major stored-grain pests and we compared it with the efficacy of the standard EC formulation. Insect mortality of adults of two primary colonizers, *S. granarius* and *R. dominica*, and one secondary colonizer, *T. confusum*, on wheat grains was assessed for a storage period of seven months. The progeny production of the test insects on the treated commodity was also assessed for both formulations and for the same storage intervals. Moreover, the decline of residues of the two pirimiphos-methyl formulations on wheat grains was assessed over time.

2. Materials and methods

2.1. Test insects

The insect species evaluated in this experiment were *S. granarius*, *R. dominica* and *T. confusum*. All species were reared at the Laboratory of Entomology and Agricultural Zoology, Department of Agriculture, Crop Production and Rural Environment, University of Thessaly, at 25 °C, 65% relative humidity (r.h.) and continuous darkness. *Sitophilus granarius* and *R. dominica* individuals were reared on whole wheat, while *T. confusum* was reared on wheat flour. For all species, adults used in the bioassays were less than 4 weeks old. Briefly, before the initiation of a bioassay, all of the adult beetles were removed from the culture, and those emerging over the next 4 weeks were used for experimentation (Hagstrum and Subramanyam, 2006).

2.2. Commodity and insecticide treatment

Untreated, clean and infestation-free durum wheat (variety Simeto) with very little dockage was used in the tests. The wheat was harvested from a local farm in June 2011. Before the experiment, wheat was kept in cold storage at −20 °C for at least two weeks. The initial moisture content of wheat, as determined by a Multitest moisture meter (Multitest, Gode SAS, Le Catelet, France) after the removal from the cold room was 13.5%.

The pirimiphos-methyl formulations tested were Actellic 50 EC (48% active ingredient [A.I.]) and Actellic 300 CS (30% A.I.). The insecticides were applied on the grains by using a Kyoto BD-183K airbrush (Grapho-tech, Japan), in order to spray at the different rates (see below).

2.3. Bioassays

Lots of 7 kg of wheat were sprayed with each of the two pirimiphos-methyl formulations at two doses, 2 and 4 mg kg^{-1}, using different lots for each formulation and dose. These doses were chosen, as they were previously shown to provide efficient control directly after application against a broad spectrum of stored-product insect species (Rumbos et al., 2013). Spraying solutions were prepared by diluting appropriate aliquots of the EC (0,1 and 0,2 ml for 2 and 4 mg kg^{-1}, respectively) and the CS (0,165 and 0,33 ml for 2 and 4 mg kg^{-1}, respectively) formulations in 25 ml of distilled water. Afterwards, wheat was sprayed by using a total volume of 1 ml of spraying solution per kg of grains. An additional series of lots were sprayed with distilled water and used as controls. Then, the grains were placed in a glass jar and shaken manually to achieve equal distribution of the insecticide in the entire grain mass. The treated grain quantities and untreated control were kept at 25 °C, 65% r.h. and continuous darkness. Plastic cylindrical vials (3 cm in diameter, 8 cm in height) were the experimental units for the tests. The top one quarter of the internal part of each vial was covered by Fluon (Northern Products, Woonsocket, USA) to prevent insects from escaping. Samples were taken from each jar at the day of application and every 4 weeks for 7 consecutive months (8 bioassays in total). Each vial was filled with 20 g of wheat and then twenty adults of mixed sex were placed into each vial, with separate vials for each species. Mortality of the exposed individuals was assessed after 7, 14 and 21 d for all beetle species. There were three replicates for each treatment (three vials), whereas the same procedure was repeated three times (three series of vials) by preparing new spraying solutions and lots of treated and untreated grains each time ($3 \times 3 = 9$ vials for each treatment).

2.4. Progeny production counts

After the final mortality count, all adults (dead and alive) were removed from the vials, and the vials were left in the incubators for an additional period of 65 d, at the same conditions as above. After the termination of this interval, the emerged individuals (adults in the case of *S. granarius* and *R. dominica*, as well as adults and larvae in the case of *T. confusum*) in each vial were counted.

2.5. Residues analysis using HPLC

Apart from the bioassays, wheat samples were taken from each jar to determine the pirimiphos-methyl residues over time. Samples of 20 g each were taken in triplicate, filled in separate vials and kept in cold storage at −20 °C until the termination of the