Nontarget Activity of Chlorpyrifos and Hydrolysis Products on *Sclerotium rolfsii*

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ABSTRACT

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The insecticide chlorpyrifos (technical), two formulations (15G and 4EC); two hydrolysis products (3,5,6-trichloro-2-pyridinol and 2-methoxy 3,5,6-trichloropyridine); the stabilizer (γ-butyrolactone); and the clay carrier were evaluated and compared with PCNB 10G for their activities in reducing radial growth, sclerotial initials formation, and germination of mature sclerotia of *Sclerotium rolfsii*. The hydrolysis product 3,5,6-trichloro-2-pyridinol, the most active chlorpyrifos-related material tested, reduced radial growth at concentrations of ≥1 μg/ml, sclerotium formation at 1–25 μg/ml, and sclerotial initials formation and sclerotial germination at 1–10 μg/ml. At a concentration of 25 μg/ml, 3,5,6-trichloro-2-pyridinol equaled PCNB in its antifungal activity. The chlorpyrifos technical and 15G and 4EC formulations were less active than 3,5,6-trichloro-2-pyridinol (listed in increasing order of activity). The other materials were not active. Implications of antifungal activity of an insecticide and dynamics of hydrolysis in soil are discussed.

Several researchers have reported antifungal activity of nematicides and insecticides on soilborne pathogens (1,5,8–11). Backman and Hammond (1) and Hammond et al (5) showed that chlorpyrifos emulsifiable concentrate suppressed growth of *Sclerotium rolfsii* Sacc. in vitro and reduced southern stem rot of peanut in the field. They demonstrated a synergism in suppression of *S. rolfsii* with the active and inert ingredients in the emulsifiable formulation and discussed the usefulness of the insecticide chlorpyrifos in an integrated pest management program on peanuts. They concluded that the granular formulation would be less active since the emulsifier is absent from that formulation. The emulsifiable concentrate formulation is no longer recommended for peanuts because of potential phytotoxicity problems, but the granular formulation is recommended for control of several peanut insects (12).

In light of the work done by Backman and Hammond (1) and the recommended use of granular chlorpyrifos on peanuts in Georgia, further investigations on the fungicidal activity of that insecticide were warranted. Formulations of chlorpyrifos, the clay carrier, the stabilizer, and two major hydrolysis products of chlorpyrifos were evaluated and compared with PCNB for their antifungal activity against *S. rolfsii*.

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MATERIALS AND METHODS

An isolate of *S. rolfsii* originally isolated from dying peanut in Tift County, GA, in 1979 was used in this study. Moistened oat or ryegrass seed was autoclaved in 250-ml flasks at 121 C for 20 min for two consecutive days. Flasks were inoculated with 4-mm cork borer plugs of *S. rolfsii* from 1-wk-old potato-dextrose agar (PDA) plates and incubated for 1 wk in an unlighted incubator at 27 C. Sclerotia were produced on PDA and air-dried before use.

Materials tested were chlorpyrifos technical (100%); montmorillonite clay carrier; 3,5,6-trichloro-2-pyridinol (99%) and 2-methoxy 3,5,6-trichloropyridine (99.9%), hydrolysis products of chlorpyrifos; γ-butyrolactone (100%), the stabilizer; and chlorpyrifos 4EC and 15G, all obtained from Dow Chemical, Midland, MI. PCNB 10G was obtained from Olin Corp., Little Rock, AK.

Water agar was amended with specific concentrations of test materials after being cooled to 45 C and thoroughly mixed, then 10-cm petri plates were poured and allowed to gel. Chemicals were evaluated at 1, 2, 5, 10, 25, and 100 μg a.i./ml in most tests; some materials were evaluated additionally at 0.5 μg a.i./ml. Granular materials were ground with a mortar and pestle before being added to the agar. Ten petri plates for each concentration of each treatment were inoculated with *S. rolfsii* by placing a single, infested seed in the center of each plate. Sclerotial germination was tested by placing 10 sclerotia on each of 10 plates per treatment on amended water agar plates. Petri plates were placed in plastic bags and incubated for 72 hr at 27 C in the dark. Average radial growth and sclerotial germination for each of 10 replicates per treatment were recorded. Numbers of sclerotia and sclerotial initials formed were recorded 3 wk after inoculation. Data were subjected to analysis of variance and Duncan's multiple range test.

RESULTS

The major chlorpyrifos hydrolysis product, 3,5,6-trichloro-2-pyridinol, was

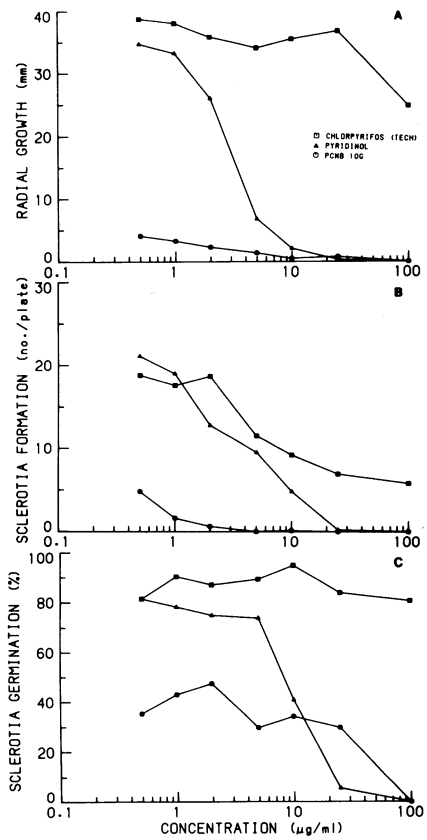

Fig. 1. Antifungal activity of chlorpyrifos technical, 3,5,6-trichloro-2-pyridinol, and PCNB 10G on *Sclerotium rolfsii*. Effect on **(A)** radial growth, **(B)** sclerotium formation, and **(C)** sclerotial germination.

the most active of the chlorpyrifos-related chemicals tested. It reduced radial growth of *S. rolfsii* at concentrations ≥1 μg/ml ($P = 0.01$), sclerotial germination at concentrations ≥1–10 μg/ml ($P = 0.01$), sclerotium formation at ≥1–25 μg/ml (Figs. 1–3), and sclerotial initials formation at ≥1–20 μg/ml, depending on test.

In contrast, the parent material, chlorpyrifos technical, reduced radial growth of *S. rolfsii* only at concentrations of 25 and 100 μg/ml (Figs. 1–3), sclerotium formation at 1–5 μg/ml ($P = 0.05$), and sclerotial initials formation at 5–100 μg/ml ($P = 0.05$). Sclerotial germination was not reduced by any concentration of chlorpyrifos technical tested ($P = 0.01$).

Both 15G and 4EC formulations of chlorpyrifos were more active than chlorpyrifos technical but not as active as 3,5,6-trichloro-2-pyridinol. Concentrations of chlorpyrifos 15G ≥10 μg/ml and chloryprifos 4EC ≥5 μg/ml reduced radial growth of *S. rolfsii* ($P = 0.01$) (Fig. 4). Sclerotium formation was reduced by all concentrations of chlorpyrifos 15G and 4EC in one test ($P = 0.01$) (Fig. 4) and by concentrations of chlorpyrifos 15G ≥10 μg/ml in another ($P = 0.05$) (Fig. 2). Sclerotial initials formation was reduced erratically by chlorpyrifos 15G at concentrations ranging from 2 to 100 μg/ml, depending on the test, and by chlorpyrifos 4EC at ≥1 μg/ml. Sclerotial germination was reduced by chlorpyrifos 15G and 4EC at 100 and 10 μg/ml, respectively. PCNB 10G at comparable concentrations was significantly more active than either formulation of chlorpyrifos for all parameters tested.

The stabilizer (γ-butyrolactone), the clay carrier, and a breakdown product (2-methoxy 3,5,6-trichloropyridine) were inactive in reducing radial growth of *S. rolfsii*, sclerotium formation, and sclerotial germination (Figs. 2 and 3). The clay carrier and 2-methoxy 3,5,6-trichloropyridine inhibited sclerotial initials formation erratically, but γ-butyrolactone did not inhibit formation.

DISCUSSION

The major breakdown product of chlorpyrifos is 3,5,6-trichloro-2-pyridinol (6); however, 2-methoxy 3,5,6-trichloropyridine is also produced in soil, probably by transformations by microorganisms. Other products of hydrolysis have been reported from in vitro studies (6), but these materials are formed in low quantities in soil and are unstable.

Because the hydrolysis product 3,5,6-trichloro-2-pyridinol is the only chlorpyrifos-associated product that demonstrated substantial activity against *S. rolfsii*, its formation in soil would be of prime importance in understanding and developing strategies for controlling disease caused by *S. rolfsii*.

Decomposition of chlorpyrifos increases with increase in soil temperature. The insecticide is most stable in organic muck soils and least stable in high-clay soils. Its stability is intermediate in sandy soil (2,7). Both hydrolysis and volatilization contribute to the dissipation of chlorpyrifos from soils. Getzin (4) showed that on air-dried Sultan silt loam at 35 C and 30% RH, chlorpyrifos was hydrolyzed to 3,5,6-trichloro-2-pyridinol at a rate three times higher (74%) than on the same soil at the same temperature at 91% RH. Chlorpyrifos volatilized at a rate three times higher (71%) at 91% RH than at 30% RH at the same temperature. This data suggests that under hot and dry conditions, chlorpyrifos dissipation would be due primarily to hydrolysis to 3,5,6-trichloro-2-pyridinol, and under wet conditions, to volatilization. The parent material is the most volatile, and 3,5,6-trichloro-2-pyridinol is relatively nonvolatile.

Accumulation of 3,5,6-trichloro-2-pyridinol is favored under hot, dry conditions in a high-clay soil if only physical aspects of degradation are taken into account. Getzin (3) and Miles et al (7)

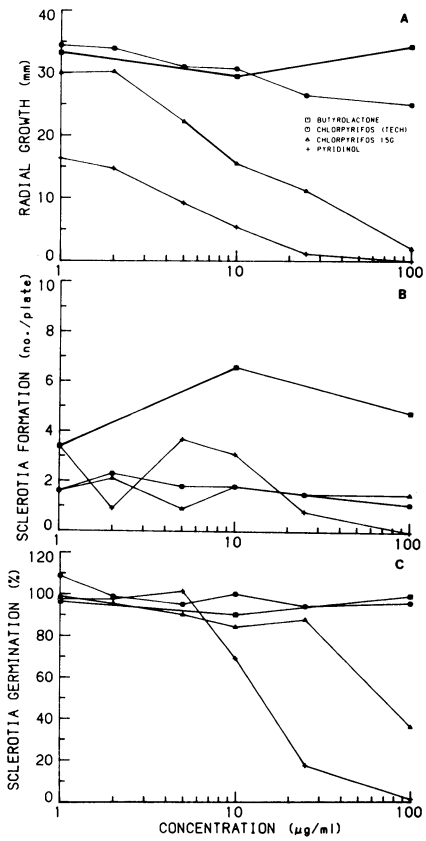

Fig. 2. Antifungal activity of γ-butyrolactone, chlorpyrifos technical, chlorpyrifos 15G, and 3,5,6-trichloro-2-pyridinol on *Sclerotium rolfsii*. Effect on **(A)** radial growth, **(B)** sclerotium formation, and **(C)** sclerotial germination.

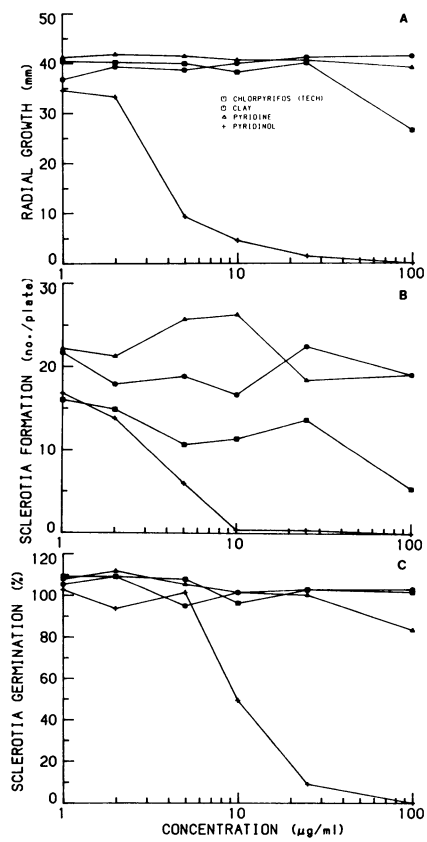

Fig. 3. Antifungal activity of chlorpyrifos technical, 2-methoxy 3,5,6-trichloropyridine, clay carrier, and 3,5,6-trichloro-2-pyridinol on *Sclerotium rolfsii*. Effect on **(A)** radial growth, **(B)** sclerotium formation, and **(C)** sclerotial germination.

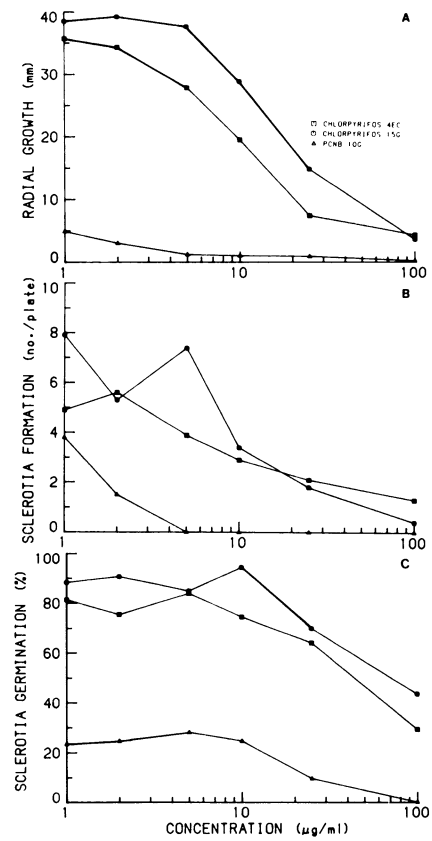

Fig. 4. Antifungal activity of chlorpyrifos 15G, chlorpyrifos 4EC, and PCNB 10G on *Sclerotium rolfsii*. Effect on **(A)** radial growth, **(B)** sclerotium formation, and **(C)** sclerotial germination.

demonstrated, however, that hydrolysis of chlorpyrifos to 3,5,6-trichloro-2-pyridinol occurred to a greater degree in nonautoclaved soils than autoclaved soils in in vitro studies. Microorganisms apparently influence the hydrolysis of chlorpyrifos.

Smiley (10) documented the control of Curvularia blight on turf with chlorpyrifos, but in laboratory studies, he failed to demonstrate toxicity to *C. lunata* with either chlorpyrifos or the solvent. The breakdown product of chlorpyrifos may be affecting the control of the disease.

Backman and Hammond (1) reported a synergism between chlorpyrifos and inert ingredients in the 4EC formulation on radial growth of *S. rolfsii*. Our study indicates that the hydrolysis product 3,5,6-trichloro-2-pyridinol—and not the parent compound—has the greatest activity. The formulated materials have intermediate activities between chlorpyrifos technical and 3,5,6-trichloro-2-pyridinol. Inert ingredients in the formulated product may act as a catylyst for hydrolysis of chlorpyrifos to 3,5,6-trichloro-2-pyridinol and thus provide antifungal activity.

Because 3,5,6-trichloro-2-pyridinol is formed under hot, dry conditions, accumulation of the hydrolysis product would not occur during periods that favor southern stem rot development. Best control of *S. rolfsii* theoretically would occur if hot, dry periods were separated by hot, moist conditions of short duration when the fungus became active. Data on formation and germination of sclerotia also indicate that 3,5,6-trichloro-2-pyridinol and formulated chlorpyrifos, to a lesser degree, would help suppress formation of these important overwintering propagules.

Only recently has the antifungal activity of chlorpyrifos been demonstrated commercially possible (1,5). With the knowledge of the toxic moiety of the chlorpyrifos activity, considerations on how best to capitalize on its activity will require further work.

ACKNOWLEDGMENTS

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