Esfenvalerate Residue Accumulation on Peanuts, Cocoa Beans, and Tobacco during a Simulated Storage Season[1,2]

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ABSTRACT Farmers stock peanuts, bagged cocoa beans, exposed tobacco, and boxed tobacco were exposed to daily applications of 0.02 g AI esfenvalerate per 28.3 m^3 (1,000 ft^3) for 235 consecutive days. Residue accumulation on peanut shells and peanut kernels ranged from 0.2 - 22.9 ppm and 13.1 - 189.6 ppb, respectively. The bag containing the cocoa beans apparently trapped most of the insecticide residue, and residues on whole beans and roasted nibs ranged from 10.4 - 452.2 and 9.6 - 118.5 ppb, respectively. Residue accumulation on exposed tobacco ranged from 0.2 - 31.1 ppm, but residues on boxed tobacco were above minimum detectable levels on only 2 of 11 sample dates.

KEY WORDS Esfenvalerate, residue, peanuts, cocoa beans, tobacco, storage.

The organophosphate insecticide dichlorvos has been used as an aerosol to control insect pests in a variety of stored product environments, including bulk peanut storages, processed food warehouses, and tobacco storages. Insecticide delivery systems are connected to a timer so that the aerosols can be applied with minimal exposure to workers. Aerosol systems inside peanut storages can be activated daily during storage, while the systems in food and tobacco storages are activated weekly or on an as needed basis. The application rate is 0.5 to 2.0 g AI per 28.3 m^3 (1,000 ft^3).

In recent years there have been concerns regarding the effectiveness and safety of dichlorvos. Indianmeal moth, *Plodia interpunctella* (Hübner), and almond moth, *Cadra cautella* (Walker), and red flour beetle, *Tribolium castaneum* (Herbst) populations in peanut storages may be developing resistance to dichlorvos (Halliday et al. 1988, Arthur et al. 1988). Several tobacco companies have voluntarily discontinued the use of dichlorvos, and the status of dichlorvos is threatened by possible regulatory action. Dichlorvos has a high mammalian toxicity; the oral and dermal LD_{50} in rats is 56 and 75 mg/kg, respectively, and even though worker exposure is minimal there are safety considerations.

The only labeled aerosol alternative to dichlorvos is synergised pyrethrins, but sufficient supplies of formulated material are often unavailable and there are questions regarding the efficacy of synergised pyrethrins. One possible replacement for dichlorvos is the S isomer of the pyrethroid fenvalerate

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[2] This paper reports the results of research only. Mention of a pesticide or a commercial or proprietary product does not constitute a recommendation or endorsement by the U. S. Department of Agriculture.

(esfenvalerate), which has an oral and dermal LD_{50} of 431 and 5,000 mg/kg, respectively. Fenvalerate is labeled for a variety of field crops, fruits, and ornamentals. A previous test established that an application rate of 0.02 g AI per 28.3 m^3 esfenvalerate, which is considerably less than the application rate for dichlorvos, would control the major insect pest species of stored peanuts and stored tobacco (Arthur and Gillenwater 1990). Topical application studies by Benezet et al. (1988) also show that fenvalerate is highly toxic to the cigarette beetle, *Lasioderma serricorne* (F.), the major insect pest of stored tobacco. The purpose of this study was to determine residue accumulation on peanuts, tobacco, and cocoa beans when esfenvalerate was applied daily at 0.02 g AI per 28.3 m^3 under simulated storage conditions.

Materials and Methods

This study was conducted in a 232.3 m^3 room at the Stored Product Insects Research and Development Laboratory, Savannah, GA. The floor of this room measured 8.8 by 6.2 m. Approximately 4.1 kg farmers stock peanuts were weighed into each of 33 cardboard boxes measuring 30 by 30 cm with a height of 15 cm. These boxes were set in 3 rows on the floor, 11 boxes per row down the length of the room. Approximately 0.9 kg of whole cocoa beans in each of 33 burlap bags constructed from larger bags commonly used to store cocoa beans were placed next to the peanut boxes. Two 10.2 by 10.2 cm plugs of flue-cured tobacco, one in a cardboard box and one exposed, were placed beside the peanut boxes and the cocoa beans.

Eight 2.3 kg cylinders were formulated by Technical Products Corporation, and each cylinder contained 0.25% esfenvalerate, 1.25% piperonyl butoxide, 18.50% oil solvent, and 80.00% p11 and p12 propellant (50/50 mixture). Technical Products also supplied a TA-5 Maxirex BD1 timer for the experiment. A double nozzle was installed on the first cylinder used in the test, and after the cylinder was calibrated it was mounted on one of the side walls, approximately 3.1 m from the floor. One nozzle was positioned between rows 1 and 2 and the other nozzle was positioned between rows 2 and 3. The cylinder was hooked to the timer, which was set to operate at 1800 hrs for 26 sec. This gave a daily application rate of 0.02 g [AI] esfenvalerate per 28.3 m^3.

The experiment was initiated on 20 April 1989, and all three commodities were sampled after 1, 8, 22, 43, 69, 97, 123, 151, 179, 207, and 235 days of daily esfenvalerate application. Peanuts were sampled by randomly selecting one box from each row on each sample date and removing the top 7.5 cm layer. A mechanical sheller was used to provide 0.9 liter samples of peanut hulls and peanut kernels, which were then frozen at -17.6 $^\circ$C until they were analyzed for residue. After a box was sampled, it was discarded. The cocoa beans from each position were divided into two lots. One was frozen at -17.6 $^\circ$C as whole beans. The other lot was baked at 163°C for 15 minutes and the skins were removed from the nuts (hereafter referred to as nibs) before they were frozen. The tobacco in the boxes was removed and frozen at the same temperature, along with the tobacco in the open position.

The cylinder was also weighed at each sample date and at selected intervals between dates. When the contents of the cylinder were low a new cylinder was installed. The cylinders were changed on day 43 (2 June), but the new cylinder failed to operate properly. This malfunction was not detected until the cylinder was weighed on 20 June. The series was sampled as planned, and the samples include the 18-day gap when the cylinder was not operating (2-20 June).

Esfenvalerate Residue Analysis

Peanuts and Cocoa Beans. All individual samples were ground in a blender. A 20 g ground sub-sample was added to 100 mL acetonitrile, then shaken for 4 hrs on a wrist-action shaker. After the sample was filtered, a 20 mL aliquot was extracted with 50 mL petroleum ether and 250 mL 2% NaCl. The petroleum ether layer was washed twice with 50 mL distilled water and dried with Na_2SO_4. Twenty g (40 mL) Florisil with 0.5% H_20 and 2.54 cm Na_2SO4 were added to a 2.2 cm inside diameter chromatographic column and washed with petroleum ether. The dried sample was added to the column and washed with first with 100 mL petroleum ether then with 40 mL 4% isopropyl alcohol (IPA) in petroleum ether. The sample was eluted with 120 mL 4% IPA in petroleum ether, evaporated to dryness under N_2, then dissolved in isooctane to make an exact volume of 5 mL. Esfenvalerate residues were determined using a gas chromatograph equipped with an electron capture detector. Four microliters were injected onto 5% ov 101 in a 2 mm by 2 mm inside diameter glass column. The temperatures of the injection port, detector, and oven column were 320, 370, and 265 °C, respectively. The column press was 38 psig and N_2 was used as the carrier. Esfenvalerate recoveries on peanut shells and peanut kernels averaged 66.3 ± 2.5 and 62.5 ± 2.7%, respectively. Esfenvalerate recoveries on whole cocoa bean nuts and roasted nibs averaged 57.4 ± 1.8 and 57.0 ± 1.8%, respectively.

Tobacco. All individual samples were ground in a blender. A 10 g sample was added to 100 mL acetonitrile, then shaken for 4 hrs on a wrist-action shaker. After the sample was filtered, a 25 mL aliquot was extracted with 15 mL hexane. The acetonitrile layer was then extracted with 50 mL petroleum ether and 250 mL 2% NaCl. The aqueous layer was discarded and the petroleum ether layer was washed twice with 50 mL distilled H_20, then dried with Na_2SO_4. Twenty g (40 mL) Florisil with 0.5% H_20 and 2.54 g Na_2SO_4 were added to a 2.2 cm inside diameter chromatographic column and washed in petroleum ether. The dried sample was added to the column and washed first with 100 mL petroleum ether and then with 40 mL 4% IPA in petroleum ether. The sample was eluted with 120 mL 4% IPA in petroleum ether, evaporated to dryness under N_2, and dissolved in 2.0 mL acetonitrile. Three mL H_20 were then added and a Fisher C-18 Prep Sep column was prepared by washing first with 2 mL acetonitrile then with 2 mL 30% acetonitrile in H_20. The sample was added and washed with 2 mL 30% acetonitrile in H_20, washed with 5 mL 60% acetonitrile in H_20, and eluted with 5 mL 80% acetonitrile in H_20. The sample was evaporated to dryness under N_2 and dissolved in isooctane to make an exact volume of 5 mL. Esfenvalerate residues were determined using the gas chromatograph described in the section for peanuts and cocoa beans. Esfenvalerate recoveries on untreated tobacco averaged 70.7 ± 1.7%. Results were analyzed using the general linear model (GLM) procedure of the Statistical

Analysis System (SAS Institute 1987) to determine mean residues (± SEM) on each sample date. The GLM procedure was also used to fit linear equations to the degradation data for each of the three commodities.

Results

Esfenvalerate residues on all three commodities increased linearly during the study and the accumulation can be described by linear regression (Figs. 1-3). Residues on peanut shells increased from day 1 to day 179 (1 April to 20 October), then declined during the final 2 months (Fig. lA). Residues increased by only 0.5 ppm from day 47 - 69 (2 June - 20 June), possibly because the sprayer was not operating during this time. The greatest percentage increase occurred between day 97-123 (28 July-25 August), when residues increased more than 100%. Maximum shell residues of 22.9 ± 1.9 ppm occurred on day 179 (20 October (day 179). Esfenvalerate residues on peanut kernels also increased during the study, but most of the residues from the daily applications were absorbed by the shell (Fig. lB). Residues increased to a maximum of 190 ± 15.1 ppb on day 107 (17 November) then declined to 138 ± 4.2 ppb on day 235 (15 December). Kernel residues on day 235 were less than those recorded for the previous 4 months.

Esfenvalerate residues on whole cocoa beans were not as great as those on peanut shells (Fig. 2A). Most of the insecticide spray was probably absorbed by the burlap bag containing the beans. Residues increased during the study, and the maximum of 452.0 ± 17.2 ppb occurred on day 235. As expected, less residue was detected on roasted nibs than on whole beans (Fig. 2B). Nib residues ranged from 10.4 to 27.5 ppb from day 1-123, and the maximum of 119 ± 14.3 ppb occurred on day 235.

During the final three months of the test, more esfenvalerate residues were detected on open exposed tobacco than on either peanut shells or whole cocoa beans (Fig. 3A). Average residues after 179, 207, and 235 days of daily application were 31.1 ± 2.6, 29.9 ± 3.3, and 30.5 ± 1.9 ppm, respectively. Esfenvalerate residues did not accumulate on boxed tobacco, and residues were above minimum detectable levels on only 2 sample dates, days 151 and 235. Average residues on those dates were 53.2 ± 16.3 and 59.0 ± 17.2 ppb, respectively

Discussion

The results of this study indicate that esfenvalerate could replace dichlorvos as an insecticide in peanut storage facilities. Dichlorvos can be applied to farmers stock peanuts at the rate of 0.5 to 2.0 g AI per 28.3 m^3 (1,000 ft^3), and the application systems are often activated daily at either dawn or dusk, when almond moths and Indianmeal moths are most likely to fly. The dichlorvos residue tolerance on farmers stock peanuts is 2.0 ppm. In our test esfenvalerate was applied at the rate of 0.02 g AI per 28.3 m^3, and the residues on kernels did not exceed 0.2 ppm even after 235 days of daily application.

In an actual field application, esfenvalerate residues on both peanut shells and kernels may be considerably less than levels detected in our test, because esfenvalerate would be applied to the surface layer of the peanut stack. When

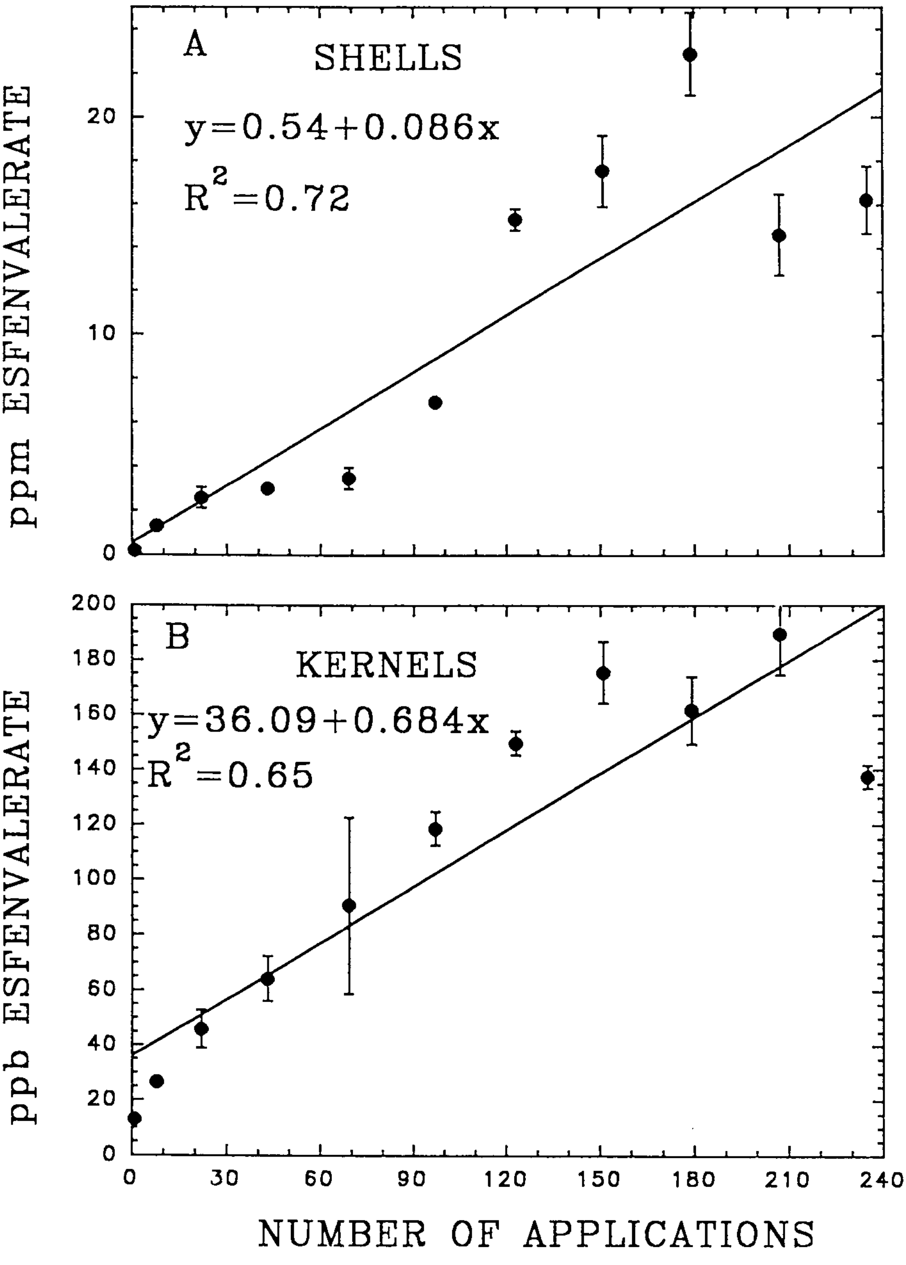

Fig. 1. Insecticide residue accumulation on peanut shells (A) and peanut kernels (B) after 1-235 daily applications of 0.02 g AI esfenvalerate per 28.2 m^3.

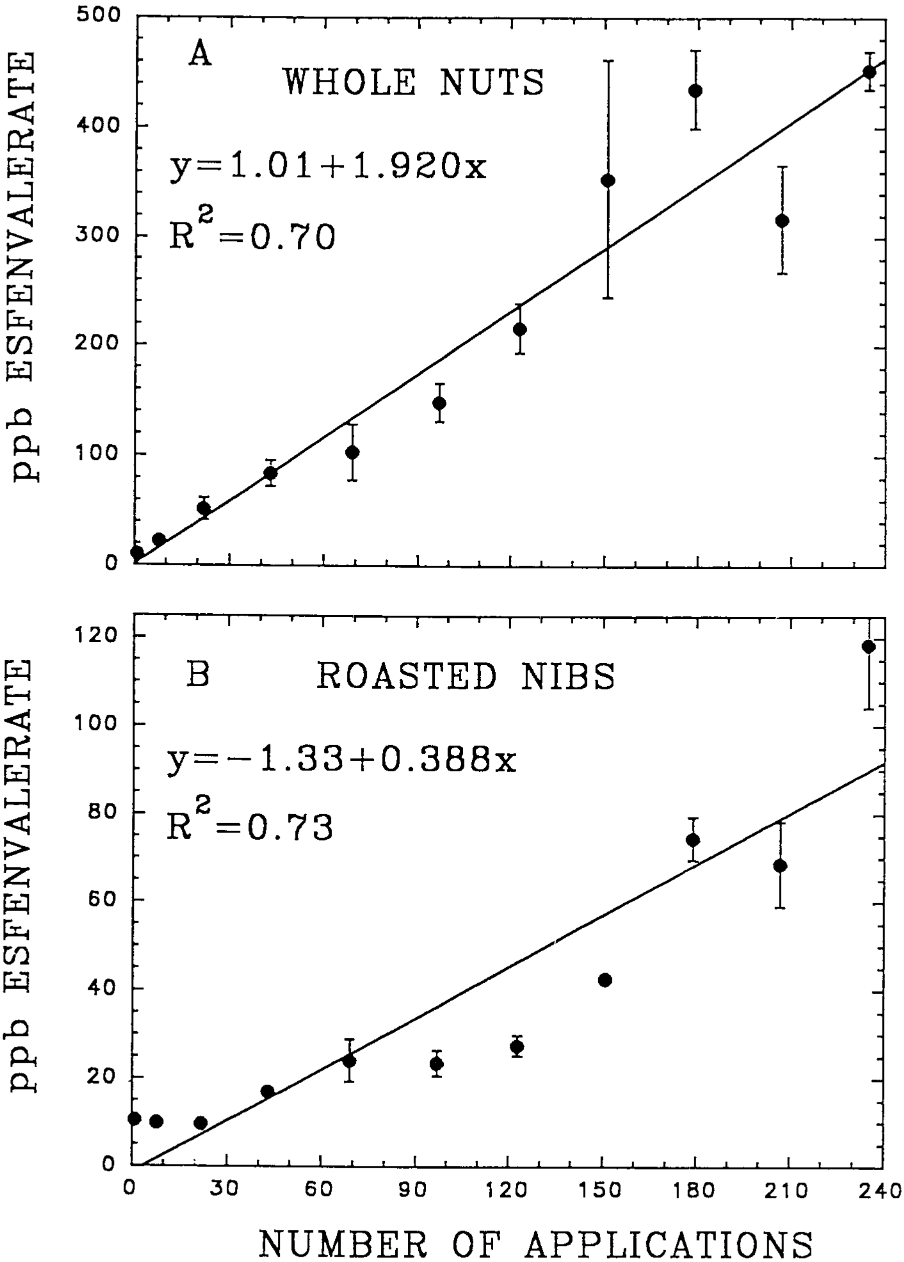

Fig. 2. Insecticide residue accumulation on bagged whole cocoa beans (A) and roasted nibs (B) after 1-235 daily applications of 0.02 g AI esfenvalerate per 28.3 m^3.

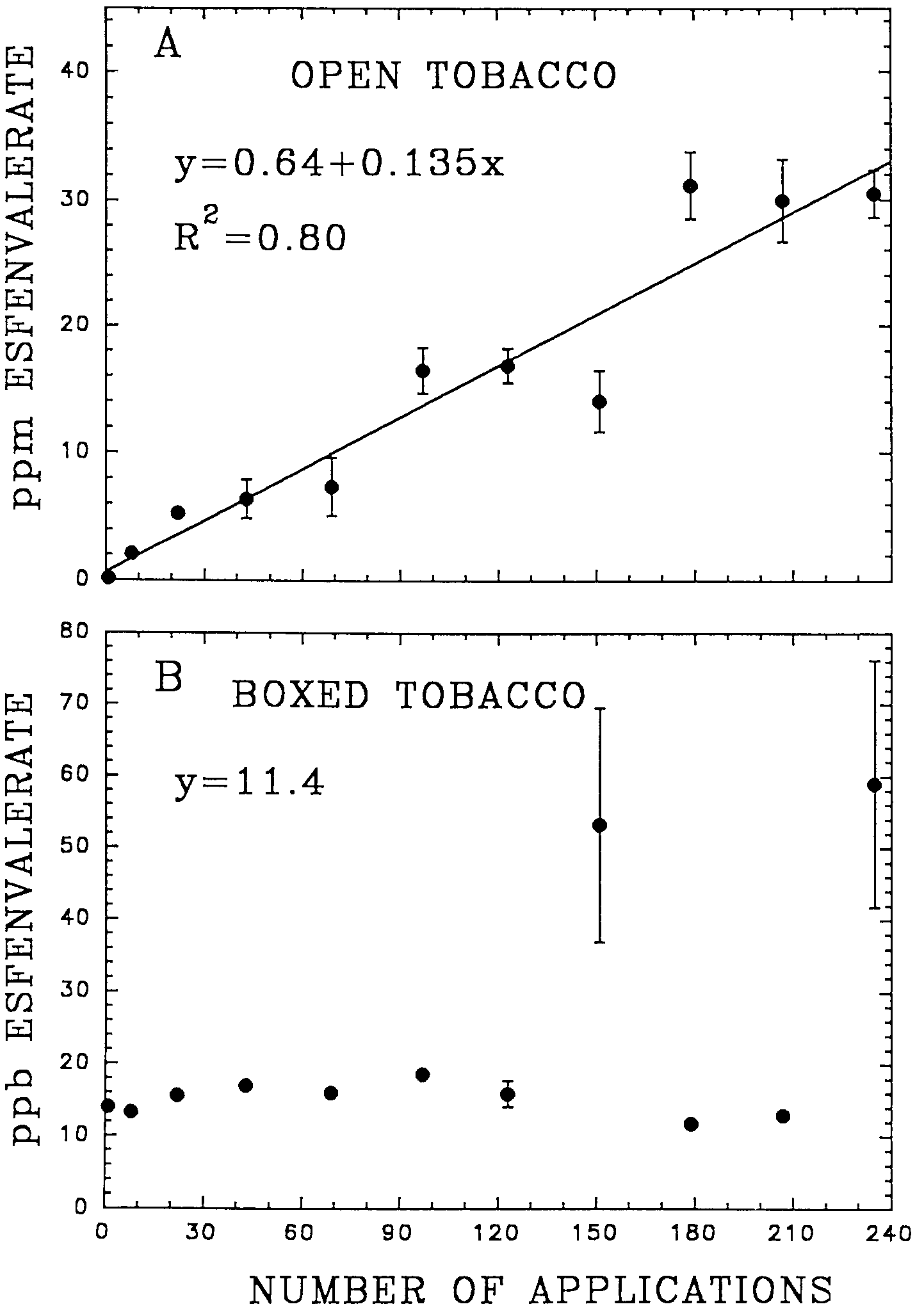

Figure 3. Insecticide residue accumulation on exposed tobacco (A) and boxed tobacco (B) after 1-235 daily applications of 0.02 g AI esfenvalerate per 28.3 m^3 (regression for boxed tobacco was not significant, $P \leq 0.05$).

peanuts are removed from the warehouse, this surface layer would be blended with the bulk of the peanuts, which could effectively distribute the insecticide residues among the bulk stack. In addition, the application rate of 0.02 g per 28.3 m^3 would control the major insect pests of stored peanuts, cocoa beans, and tobacco (Arthur and Gillenwater 1990), indicating that dichlorvos could be replaced by a less hazardous chemical that can be applied at a much lower rate and reduce residue accumulation on the finished product. Cocoa beans are usually stored in 45.5 kg (100 lb) burlap bags. Our test seems to indicate that if esfenvalerate was applied at the rate of 0.02 g AI per 28.3 m^3, most of the residue would be intercepted by the bag. We cannot answer this question with certainty because the small bags used in our test were not analyzed for residue. However, residues on whole beans did not exceed 0.5 ppm at any time during the 235 daily applications. In actual practice cocoa beans are roasted and skinned before they are processed, and the residues on roasted nibs in our test did not exceed 120 ppb. Esfenvalerate could be safely applied in cocoa bean warehouses under current management systems.

In past years dichlorvos was frequently used to control insect pests in stored tobacco, but currently many companies are voluntarily removing dichlorvos from pest management programs. Tobacco is usually stored in either cardboard boxes, hogsheads or plastic wrapping (Tersa bales) and rarely exposed as it was in our simulated study. Esfenvalerate could be used in insect pest management programs if tobacco were stored in cardboard boxes because, as our test showed, residues would not accumulate on the tobacco. The residues are likely to be trapped in the cardboard.

Acknowledgments

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