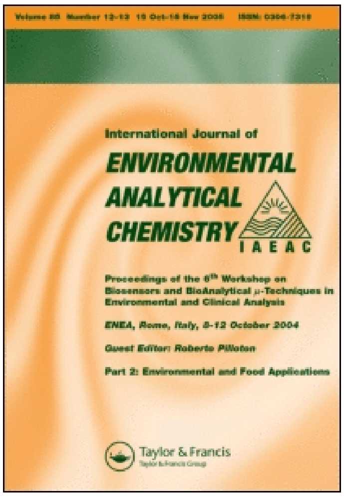

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Bay 93820 Residues: Their Determination and Persistence in Coastal Bermudagrass, Forage Corn, and Corn Silage

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Residues of Bay 93820 (isopropyl salicylate *O*-ester with *O*-methyl phosphoramidothioate) and its oxygen analog were determined in Coastal bermudagrass (*Cynodyn dactylon* (L.) Pers.), corn, and corn silage. The insecticide was applied in the field as aqueous sprays of an emulsifiable concentrate at rates of 6, 12, and 24 oz (active ingredient) per acre. Glass jar silage was made from 1-day post-field treatment corn. Residues were analyzed by gas chromatography by using a flame photometric detector sensitive to phosphorus; details of the analytical procedure are presented.

Residue levels of Bay 93820 in both corn and grass diminished to less than 1 ppm after 14 days of weathering in the field. Residues of the *O*-analog were lower than those of Bay 93820; however, they represented a much larger portion of the total residue than with any other *O*-analog-forming organophosphorus insecticide previously tested at our laboratory. Residues of Bay 93820 were essentially stable and persistent in corn silage, whereas the small amounts of *O*-analog tended to increase slightly.

INTRODUCTION

Bay 93820 (isopropyl salicylate *O*-ester with *O*-methyl phosphoramidothioate) is a product of the Chemagro Corp., Kansas City, Mo. In toxicological tests with rats, the compound had an oral LD_{50} of 50 mg/kg, a dermal LD_{50} of 200 mg/kg, and an inhalation LC_{50} of 2000 mcg/l per hr of exposure.[1]

Recently, additional tests with rats indicated an oral LD_{50} of about 39 mg/kg; toxicological data for the oxygen analog (hereafter *O*-analog) are not yet available (personal communication, Chemagro Corp.). Bay 93820 has shown promise for controlling forage insects[1] and some cotton insects;[2] it has also been tested as a molluscicide.[3]

As part of our investigation of new insecticides being developed for the control of forage insects, we examined the field persistence of Bay 93820 and its *O*-analog in two common forages grown in the southeastern United States. A modified analytical procedure for the determination of Bay 93820 and its *O*-analog, field persistence of Bay 93820 in corn and Coastal bermudagrass, *Cynodon dactylon* (L.) Pers., forage and the stability of residues of the insecticide in corn silage are presented.

EXPERIMENTAL

Spray application and field experimental sampling designs

Sprays were prepared from an emulsifiable concentrate (hereafter EC) formulation of Bay 93820 (3 lb active ingredient (hereafter ai) per gal) kindly supplied by the Chemagro Corp. Chemical analysis of the concentrate detected the following percentage contents: Bay 93820, 38.6% and *O*-analog, 0.52%. Sprays were applied at rates of 6, 12, and 24 oz (ai)/acre of the analyzed Bay 93820 content to both forage crops.

Grass

Four parallel blocks of 0.4 acre each, one each for 0, 6, 12, and 24 oz/acre insecticide treatment, separated with 50-ft buffer zones, were marked in a pasture of pure Coastal bermudagrass. Test areas consisted of one block divided into four plots (replications). Each plot, 96 × 45.5 ft, was stratified into 16 (4 × 4) subplots (sampling locations) with subplots further stratified into 9 (3 × 3) subsampling locations. Samples of grass, cut at random from a 1-ft^2 area in each subsampling location, were composited to form a plot sample for residue analysis. Each plot sample was placed in a polyethylene bag as cut and was weighed in the field. The grass, when sprayed, had 3 weeks of growth after a cutting for hay. Grass samples were taken immediately after the sprays had dried and 1, 7, 14, 21, and 28 days later.

The grass plots were treated with a conventional tractor-mounted sprayer equipped with a boom giving a 12-ft swath. The boom contained seven flat cone nozzles arranged 20.6 in. apart. The system, calibrated to deliver 25 gal of spray/acre moved at a speed of 4 miles/hr.

Corn

The ensilage corn, DeKalb-805 single cross, was planted in rows 38 in. apart and marked off into four blocks, one each for 0, 6, 12, and 24 oz/acre treatment of actual insecticide in the EC. Each block was 0.2 acre, divided into four equal-sized plots for replications per treatment. Each plot was 16 rows wide and 45.4 ft long. Sixteen corn plants were randomly cut at soil level, one per row across plots per sampling period. Plants were chopped as for silage in a mobile (10 in.) silage cutter. The chopped plants were thoroughly mixed and about 2 kg was placed in a polyethylene bag for residue analysis; it was weighed, and taken to the laboratory for processing. Samples were taken at intervals of 0, 1, 7, 14, 21, and 28 days after the insecticide treatment.

Spray treatments were applied to corn with a 6-ft high high-clearance tractor sprayer. The boom, arranged to spray four rows with two hollow-cone nozzles on each side of a row, was adjusted to give good coverage 20–24 in. above and below average ear height. Sprays were applied when plants were in full tassel and the ears in early milk stage. The system was calibrated to deliver 50 gal/acre with the sprayer moving at 4 miles/hr.

Jar corn silage

Corn silage was made in 1-qt glass jars to provide us with preliminary information on the stability of residues in corn silage media. Field-chopped corn plants, taken concurrently with and from the 1-day field samples, samples for persistence studies, were packed tightly in the jars (six per treatment level) and sealed. Three of the jars per treatment level were frozen immediately and the other three were stored for 30 days at 85°F, and then held frozen at 15°F until analyzed for residues.

Extraction and preparation of samples for analysis

The method employed for the analysis of residues of Bay 93820 and its *O*-analog was our modification of the procedure described by Thornton and Stanley.[6]

Field samples of Coastal bermudagrass or forage corn were finely chopped in a Hobart® cutter and mixed well. Twenty grams of each sample was transferred to a Soxhlet apparatus (Fisher Scientific Co., No. 9-556B) containing a plug of glass wool to prevent insoluble plant material from siphoning over during the solvent exchange. Each sample was extracted under nitrogen for 6 hr at the rate of about 10 exchanges/hr by using 150 ml of 10% methanol in chloroform containing two drops each of mineral oil and diethylene glycol to serve as a keeper. The extract was allowed to cool, then percolated through a plug of sodium sulfate (ca. 25 mm diam. × 30 mm thick) and the flask and plug were washed with 10 ml of fresh chloroform. Four more drops of diethylene glycol were added to the extract, then it was evaporated just to dryness on a water bath (35°C) under water pump vacuum. The residue was taken up in 150 ml of hexane and transferred to a 250-ml separatory funnel, then the flask was rinsed with 20 ml of methanol and finally with 80 ml of 25% aqueous sodium chloride, each of which was also added to the separatory funnel. The mixture was shaken vigorously for 30 sec, and after the layers had separated the aqueous phase (containing the *O*-analog) was drained back into the original flask. The hexane layer (containing the parent insecticide) was percolated through a plug of sodium sulfate and the funnel and plug were rinsed with 10 ml of fresh hexane. The hexane percolate was concentrated at 35°C as previously described, adjusted to 5 ml with hexane, and reserved for injection into the gas chromatograph.

The aqueous layer was again returned to the same separatory funnel and extracted three times with 25-ml portions of dichloromethane, with each portion being allowed to percolate through a plug of sodium sulfate. Four drops of diethylene glycol were added and the extract was evaporated just to dryness at 35°C as previously described.

The *O*-analog in the residue was then deaminated by adding 5 ml of acetone, 20 ml of 2N HCl and heating at 60°C for 30 min. After cooling, the mixture was transferred to a 125-ml separatory funnel by using 20 ml of distilled water and extracted twice with 25-ml portions of dichloromethane. Each portion was allowed to percolate through a plug of sodium sulfate and the plug was finally washed with 10 ml of fresh dichloromethane. Again, four drops of diethylene glycol were added to the extract and it was evaporated just to dryness as described. Residues of the deaminated *O*-analog were then methylated by adding 2 ml of diazomethane solution in ether prepared from Diazald (Aldrich Chemical Co.). Fifteen min later the solution was diluted to 5 ml with benzene for injection into the gas chromatograph.

Gas chromatographic equipment and procedure

An F & M Model 700 Gas Chromatograph (Hewlett-Packard Co., Avondale, Pa.) equipped with a Melpar Flame Photometric Detector (available from Tracor, Inc., Austin, Texas) was operated in the phosphorus mode (526-nm filter). The 45-cm glass column (4-mm ID) contained 10% OV-101 (w/w) on 80-100 mesh Gas Chrom Q® (Applied Science Lab, State College, Pa.) and was operated isothermally at 180°C and 170°C for the analysis of Bay 93820 and its *O*-analog, respectively; it was preconditioned overnight at 250°C before use. Flow rates of the gases in ml/min were: nitrogen (carrier), 160; hydrogen, 200; and oxygen, 40. The temperature of the injection port and detector was 190°C.

With the stated conditions, we injected 5 mcl of the sample for analysis of the residues. The retention times for Bay 93820 and its *O*-analog were 2.00 and 1.40 min, respectively. Typical gas chromatograms of the Bay 93820 and its *O*-analog fractions of grass are presented in Figure 1. Since chromatograms for corn and corn silage were similar to those for grass, they are not shown. Recoveries of Bay 93820 and its *O*-analog from grass, corn, and corn silage spiked at levels of 0.05 to 5.0 ppm were 93±3% and 80±3%, respectively. The sensitivity of the method was about 0.004 ppm (based on twice noise) for both compounds. The *p*-values[4,5] are useful in developing analytical methods for other substrates and for identification at the ng level; these values for Bay 93820 and *O*-analog derivative in hexane-acetonitrile were 0.016 and 0.041, respectively.

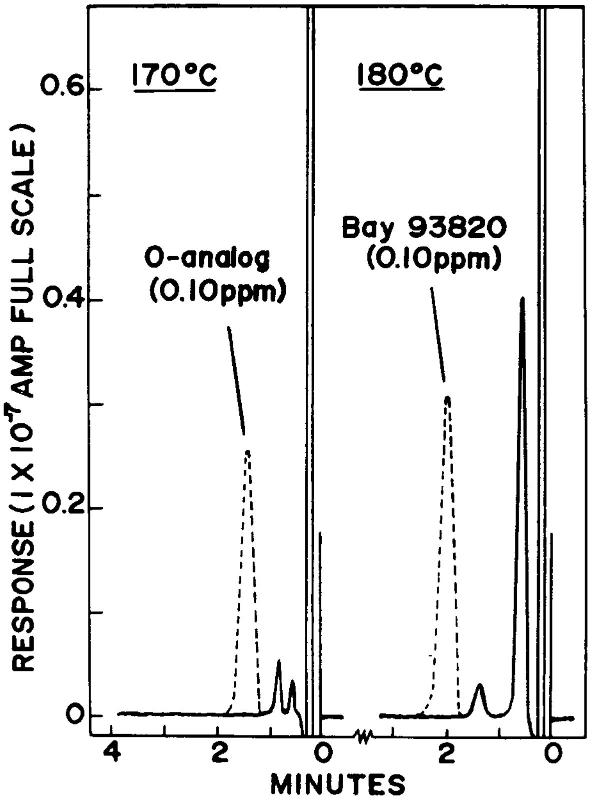

FIGURE 1 Gas chromatograms of Bay 93820 and its *O*-analog. Solid lines are unfortified controls of grass equivalent to 20 mg; broken lines are the same fractions spiked with 2 ng (0.10 ppm) of the insecticide.

RESULTS AND DISCUSSION

Residues of Bay 93820 and its *O*-analog in Coastal bermudagrass are presented in Table I. Total residues in plots treated at the highest level (24 oz/acre) declined from about 138 to 0.10 ppm during the 28 days of weathering (2.50 in. of rainfall). After 21 days, no residues (< 0.008 ppm) could be detected in grass treated with 6 oz/acre. The dissipation of both residue components from grass treated with 12 oz/acre is graphically depicted in Figure 2.

Table II lists both residue components in the corn after the various periods of weathering. Total residues in all of the treated plots declined to less than 1 ppm during the first 14 days of weathering (1.90 in. of rainfall). After 28 days of weathering, no residues could be detected in corn treated with 6 oz/acre. Figure 3 graphically illustrates the decline of both residue components in corn plots treated with 12 oz/acre.

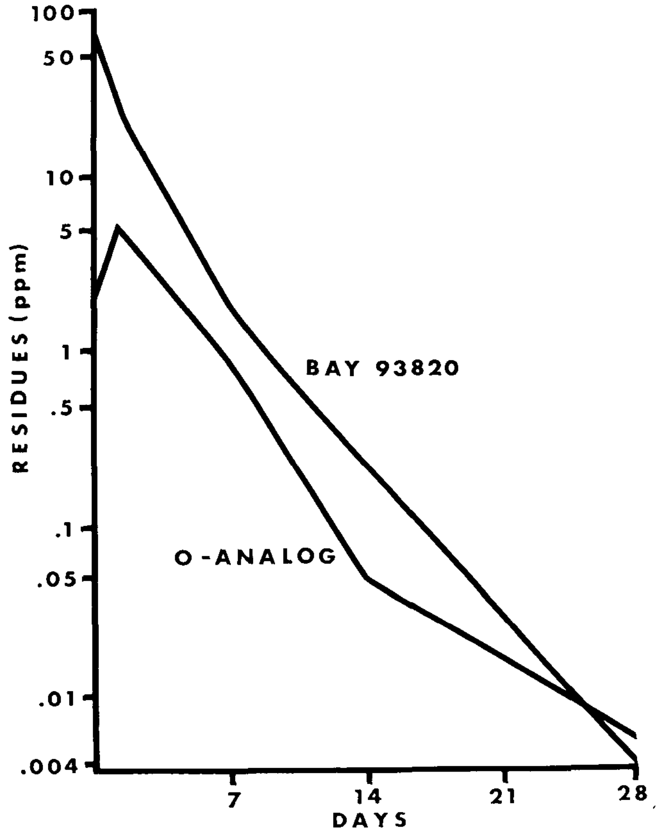

FIGURE 2 Residues of Bay 93820 and its *O*-analog in Coastal bermudagrass after spray application of 12 oz/acre.

TABLE I

Residues of Bay 93820 and its *O*-analog in Coastal bermudagrass after treatment with Bay 93820 emulsifiable concentrate at three levels. Tifton, Georgia 1970

Days post-treatment	Rainfall (in.)[a]	Treatment level (oz/acre)	Dry matter (%)	Residues (ppm, $\bar{x} \pm S_{\bar{x}}$, wet basis)[b] Bay 93820	*O*-analog	Total
0	0.00	6	32.5±0.8	26.2 ±1.1	1.50 ±0.13	27.0 ±1.2
		12	33.4±0.8	65.2 ±1.6	2.08 ±0.14	67.3 ±1.6
		24	32.6±0.8	134.0 ±2.0	4.48 ±0.30	138.0 ±1.8
1	0.00	6	32.6±1.2	9.02 ±0.83	2.28 ±0.34	11.3 ±1.1
		12	32.9±0.7	26.2 ±1.6	5.09 ±0.22	31.3 ±1.8
		24	31.5±1.1	68.3 ±3.3	8.64 ±0.54	76.9 ±3.8
7	1.90	6	30.4±0.4	0.449±0.057	0.262±0.031	0.711±0.088
		12	30.9±0.7	1.74 ±0.09	0.824±0.118	2.56 ±0.20
		24	29.8±0.4	4.60 ±0.25	1.97 ±0.33	6.57 ±0.59
14	0.25	6	30.4±0.3	0.024±0.006	0.024±0.001	0.048±0.006
		12	29.8±0.5	0.208±0.022	0.046±0.006	0.254±0.018
		24	29.6±0.4	0.710±0.052	0.247±0.039	0.957±0.076
21	0.35	6	33.6±0.8	<0.004±	<0.004±	<0.008±
		12	33.0±0.5	0.026±0.010	0.018±0.002	0.044±0.013
		24	33.8±0.9	0.216±0.044	0.068±0.014	0.284±0.057
28	0.00	6	36.2±0.4	<0.004±	<0.004±	<0.008±
		12	36.7±0.9	0.004±0.000	0.006±0.000	0.010±0.002
		24	37.8±0.5	0.067±0.021	0.034±0.006	0.101±0.027

[a] Between samplings; total = 2.50 in.

[b] Corrected for 93% recovery of Bay 93820 and 80% recovery of the *O*-analog. No residues were detected in samples taken from untreated plots at the various intervals. Each value is the mean of four samples.

TABLE II

Residues of Bay 93820 and its *O*-analog in forage corn after treatment with Bay 93820 emulsifiable concentrate at three levels. Tifton, Georgia 1970.

Days post-treatment	Rainfall (in.)[a]	Treatment level (oz/acre)	Dry matter (%)	Residues (ppm, $\bar{x} \pm S_{\bar{x}}$, wet basis)[b] Bay 93820	*O*-analog	Total
0	0.00	6	17.5±0.5	6.38 ±1.00	0.162±0.016	6.54 ±0.99
		12	17.2±0.4	12.9 ±2.3	0.318±0.068	13.2 ±2.3
		24	16.6±0.3	14.2 ±0.8	0.310±0.057	14.5 ±0.9
1	0.00	6	17.5±0.4	3.79 ±0.54	0.100±0.025	3.89 ±0.55
		12	17.6±0.1	8.86 ±0.34	0.238±0.081	9.09 ±0.29
		24	16.2±0.6	17.6 ±3.5	0.605±0.238	18.2 ±3.5
7	1.90	6	18.8±0.1	0.380±0.019	0.259±0.070	0.638±0.070
		12	18.1±0.1	0.990±0.064	0.632±0.165	1.62 ±0.21
		24	18.7±0.3	2.82 ±0.15	1.30 ±0.33	4.12 ±0.26
14	0.25	6	22.3±0.6	0.026±0.001	0.034±0.012	0.060±0.013
		12	21.0±0.8	0.076±0.011	0.133±0.042	0.208±0.041
		24	21.9±0.1	0.352±0.053	0.238±0.067	0.590±0.117
21	0.35	6	25.4±0.8	0.012±0.002	0.010±0.001	0.022±0.002
		12	24.7±0.3	0.025±0.002	0.030±0.004	0.055±0.005
		24	26.8±0.5	0.086±0.015	0.129±0.025	0.215±0.040
28	0.00	6	32.8±0.6	<0.004	<0.004	<0.004
		12	32.3±0.5	0.006±0.001	<0.004	0.008±0.002
		24	32.1±1.1	0.052±0.014	0.118±0.041	0.170±0.055

[a] Between samplings; total = 2.50 in.

[b] Corrected for 93% recovery of Bay 93820 and 80% recovery of the *O*-analog. No residues were detected in samples taken from untreated plots at the various intervals.

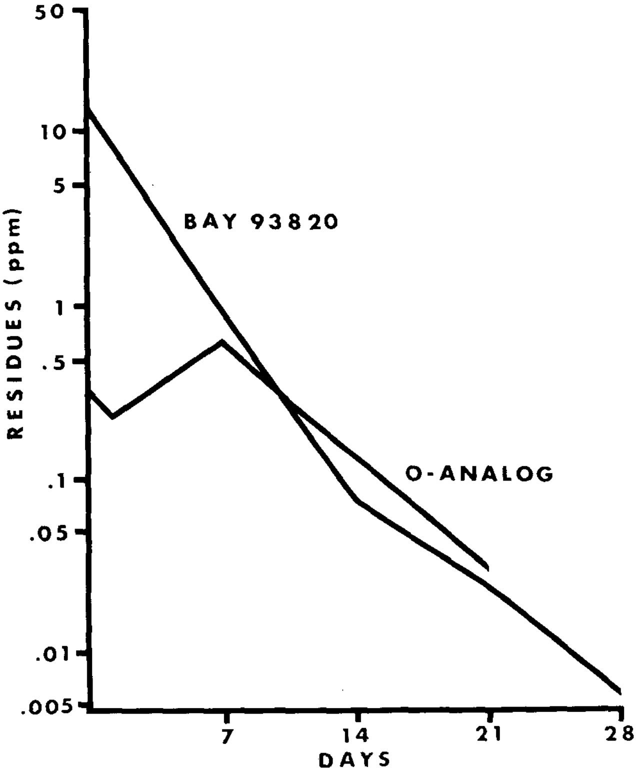

FIGURE 3 Residues of Bay 93820 and its *O*-analog found in field corn after a spray application of 12 oz/acre.

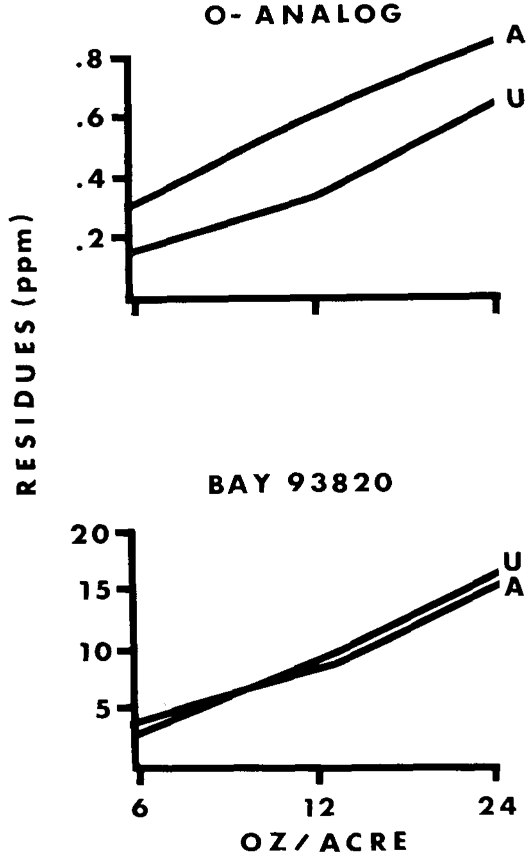

FIGURE 4 Residues of Bay 93820 and its *O*-analog in corn silage prepared in jars, ensiled 1-day posttreatment at insecticide application rates of 6, 12, and 24 oz/acre; silage aged (A) for 30 days at 85°F and unaged (U) and frozen immediately.

Results concerning the stability of Bay 93820 residues in corn silage are presented in Table III. Residues of Bay 93820 were essentially unchanged during the 30 days of ageing at 85°F, whereas the small amounts of *O*-analog tended to increase slightly. The silage residues are graphically contrasted in Figure 4.

TABLE III

Residues of Bay 93820 and its *O*-analog in corn silage (aged and unaged) prepared from field samples 1-day post-treatment with three levels of emulsifiable concentrate. Tifton, Georgia 1970.

Treatment level (oz/acre)	Dry matter (%)	Residues (ppm, $\bar{x} \pm S_{\bar{x}}$, wet basis)[a] Bay 93820	 *O*-analog	 Total
		Unaged silage		
6	16.5 ± 0.1	3.35 ± 0.24	0.162 ± 0.038	3.51 ± 0.27
12	15.5 ± 0.6	8.69 ± 0.79	0.336 ± 0.052	9.04 ± 0.75
24	15.8 ± 0.3	15.2 ± 0.8	0.655 ± 0.151	15.9 ± 0.7
		Aged silage[b]		
6	14.7 ± 0.6	3.59 ± 0.50	0.315 ± 0.051	3.90 ± 0.51
12	15.4 ± 0.6	8.33 ± 1.16	0.620 ± 0.181	8.93 ± 1.33
24	14.7 ± 0.3	15.1 ± 1.4	0.863 ± 0.116	16.0 ± 1.5

[a] No residues were detected in untreated silage.

[b] Sealed in glass jars (qt) and aged at 85°F for 30 days.

The results of these tests indicate that residues of Bay 93820 and its *O*-analog are essentially nonpersistent[7] when applied in the field to corn or Coastal bermudagrass for forage insect control. However, it should be noted that the residue level of the *O*-analog and its portion of the total residue was much higher than has been found with any other *O*-analog-forming organophosphorus insecticide tested at our laboratory.

Acknowledgements

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