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Analytical Method for Nitrapyrin and 6-Chloropicolinic Acid Residues in Strawberry Fruit and Soil

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Nitrapyrin [2-chloro-6-(trichloromethyl)pyridine], a highly specific nitrification inhibitor, is the active ingredient of N-Serve. Used as a preplant soil application at a rate of 0.5 lb of AI/acre, strawberry yields were increased by ~2.5 tons/acre. The increase was statistically significant at the 5% level for the 1977–1978 winter planting and at the 10% level for the 1978–1979 winter planting. Residue analytical methodology for nitrapyrin and its principal degradation product 6-chloropicolinic acid in strawberry fruit and soil is presented. No determinable residues of nitrapyrin (≥0.04 ppm) were detected in field-grown strawberries. The maximum level of 6-chloropicolinic acid found was 0.09 ppm in strawberries. Residue data for soil are also presented.

Nitrapyrin [2-chloro-6-(trichloromethyl)pyridine] is the active ingredient of N-Serve. It is a highly specific nitrification inhibitor, being selectively active against *Nitrosomonas*, the soil bacteria responsible for conversion of ammonium ion (NH_4^+) to nitrite ion (NO_2^-) in soil (Goring, 1962a,b). Although plants usually utilize nitrogen as nitrate (NO_3^-) for plant uptake, nitrate ion, unlike ammonium ion, is more readily leached from the soil and is lost from the soil into the atmosphere by further microbial activity which converts nitrate ion to nitrogen gases such as N_2, NO_2, and N_2O. Nitrapyrin, when added to the soil with an ammonia fertilizer such as ammonium sulfate, prevents *Nitrosomonas* from converting the ammonium ion to nitrite ion, which would be subsequently converted to nitrate ion, and thereby allows the plant greater opportunity to absorb it as NH_4^+ (Huber et al., 1977).

Efficient use of fertilizer applied is highly desirable in light of increased energy costs and to reduce water pollution by nitrate ion from agricultural runoff and leaching. Currently there is great interest in using nitrapyrin for strawberry production to obtain significantly increased yields (Welch et al., 1979). In 1979, 11 300 acres in California produced over 461 million lb of strawberries (74% of the U. S. total production) with 69% sold fresh and 31% processed (California Strawberry Advisory Board, 1980). The average production was 20.0 tons/acre, and the total crop generated revenues in 1979 of 164 million dollars (California Strawberry Advisory Board, 1980). California strawberry production is generally a 5–200-acre "small grower" operation.

Dissipation of nitrapyrin from soil (Redemann et al., 1964; Herlihy and Quirke, 1975), uptake and metabolism of nitrapyrin and 6-chloropicolinic acid (6-CPA) by plants (Redemann et al., 1965; Meikle and Redemann, 1966), metabolism of nitrapyrin by dog and rat (Redemann et al., 1966; Redemann and Clark, 1967), assay for 6-CPA residues in bovine milk (Jensen, 1971), and hydrolysis and photolysis studies of nitrapyrin and 6-CPA (Redemann and Youngson, 1968; Meikle et al., 1978) have been reported. Current tolerances for 6-CPA are 1 ppm in or on cottonseed, 0.5 ppm in or on corn fodder and forage, sorghum fodder, and wheat forage and straw, and 0.1 ppm in or on corn grain (field corn, sweet corn, and popcorn), fresh corn including sweet corn (kernels plus cob with husk removed), sorghum grain and forage, and wheat grain (Dow Chemical Co., 1977).

Reported here are strawberry yield data and residue data for nitrapyrin and its principal degradation product, 6-chloropicolinic acid, in strawberry fruit and in soil after a preplant field application of nitrapyrin added to ammonia nitrogen fertilizer.

EXPERIMENTAL SECTION

Plots and Treatments. Field plots were located at the University of California South Coast Field Station, Santa Ana (Orange County), CA. Each planting bed was 40 in. (1.0 m) wide and 15 ft (4.6 m) long and was planted with two rows of the cultivar spaced 8 in. (20 cm) apart (52 300 plants/acre). The soil was a San Emigdio (EmA) type sandy loam containing less than 0.5% organic matter and having a pH of ~7.8. Annual rainfall for the area is 12 in. (300 mm) per year.

Two commercially important varieties of strawberries, Tufts and Tioga, were each planted in separate plots which had received preplant fertilizer treatments of 21–0–0 (21% nitrogen–0% phosphorus–0% potassium) or 16–20–0, with and without added N-Serve. Thus, there were four plots treated with fertilizer and N-Serve and four corresponding plots treated with fertilizer but without added N-Serve.

N-Serve 24E (2 lb of AI/gal) was premixed with the fertilizer prior to soil incorporation and was used at a rate of 1.0 qt of formulation/acre (0.5 lb of AI/acre, 0.56 kg of AI/ha). Application was made Nov 1, 1978, by dropping the fertilizer mixture into a 6 in. (15 cm) deep slot in a continuous band on top of the planting bed (two bands/bed). The cultivar was then planted in the slot on Nov

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2, 1978. No further fertilizer was applied after the preplant application and no further cultivation was done or required. Drip irrigation was used and the soil moisture was maintained at field capacity. For further description of strawberry culture in California, see University of California (1977).

Pesticide applications for the crop consisted of preplant fumigation with a mixture of methyl bromide and chloropicrin and three treatments each consisting of Plictran (cyhexatin), Thiodan (endosulfan), Benlate (benomyl), captan, and 5% Sevin (carbaryl) bait at maximum label rates. Applications were made Nov 20, 1978 (before polyethylene mulch), Jan 20, 1979, and March 15, 1979.

Extraction of Strawberries. The procedures described herein differ signigicantly from the procedure of Jensen et al. (1978) entitled "Determination of 6-Chloropicolinic Acid in Corn, Rice and Cottonseed" but incorporate a number of their analytical steps.

Nitrapyrin. A 100-g subsample was macerated with 300 mL of acetone for 1 min in a Waring Blendor jar. The macerate was transferred to a beaker and stirred for 20 min with a magnetic stirrer. It was then vacuum filtered through a No. 1 Whatman filter in a Büchner funnel. Most of the acetone was removed from a 50-mL aliquot of the filtrate in a rotary vacuum evaporator at 35 °C. The aqueous residue was transferred to a separatory funnel and, after addition of 50 mL of 0.1 N NaOH solution and 50 mL of diethyl ether, shaken for 1 min. The aqueous phase was saved for further processing for 6-CPA. The ether was evaporatively removed from the organic phase and the residue was dissolved in hexane for GLC analysis.

6-CPA. The aqueous phase (see above) was placed in a separatory funnel and 2 mL of concentrated H_3PO_4 (85%), 20 g of NaCl, and 25 mL of ether were added and then shaken for 1 min. The aqueous phase was reextracted with another 25 mL of ether. Each ether extract was placed in a 50-mL round-bottomed flask and the ether was removed in a rotary evaporator. Then 3 mL of BF_3 in CH_3OH (14% w/v) reagent was added, and after a stopper was clamped in the flask, the mixture was heated for 1 h at 65 °C. After being cooled, the solution was transferred to a graduated centrifuge tube with 5 mL of 10% aqueous Na_2SO_4 and 5 mL of benzene. After being stoppered, the tube was shaken for 1 min. The benzene phase was analyzed for methyl 6-chloropicolinate by GLC.

Procedural Recovery. Samples were fortified just prior to the blending step by addition of analytical standards in organic solvent to the macerated strawberries in the Waring Blendor jar. Mean recoveries and standard deviations (three samples) after fortification with 1.0, 0.5, and 0.1 ppm were 94 ± 3, 86 ± 4, and 83 ± 1%, respectively, for nitrapyrin and 84 ± 4, 77 ± 2, and 85 ± 2%, respectively, for 6-CPA.

Total 6-CPA Residues. A 200-g sample of berries was macerated in a Waring Blendor jar. A 25-g aliquot was refluxed with 50 mL of 6 N HCl for 2 h. The solution was then adjusted to about pH 1 by slowly adding 10 g of NaOH pellets. The mixture was vacuum filtered and the filter pad rinsed with 10 mL of water. The filtrate and 10 g of NaCl were placed in a separatory funnel, and the mixture was extracted twice by using 50 mL of ether and a 1-min shaking time. Each ether extract was placed in a 100-mL round-bottomed flask and the ether was removed by using a rotary evaporator. The residue was derivatized with BF_3–CH_3OH as described above for 6-CPA residues.

Procedural Recovery. 6-Chloropicolinamide (6-CP-Amide) was synthesized to serve as a model compound for any conjugates that might be present to test the procedure. The rationale was that conditions effective for hydrolyzing the amide would be suitable for hydrolyzing 6-CPA conjugates. The amide was prepared by the action of ammonium hydroxide solution on the acid chloride which was prepared by treating the acid with thionyl chloride. The R_f values for the acid and amide on 100 μm thickness silica gel TLC plates were 0.43 and 0.81, respectively, in a 1:9 (v/v) concentrated ammonium hydroxide solution–absolute ethanol solvent system.

The mass spectrum of 6-chloropicolinamide (mp 140–141 °C) was obtained at ambient temperature and by using 70 eV and 0.30 μA. The m/e and relative intensity values (in parentheses) were 158 (0.23), 156 (0.65), 115 (0.37), 114 (0.17), 113 (1.00), and 112 (0.31), 78 (0.57), 77 (0.10), and 76 (0.38); m/e values representing less than 10% of the base peak are not reported. The 156 and 158 m/e values correspond to the parent compound with ^{35}Cl and ^{37}Cl isotopes, respectively. Loss of CONH yields m/e values of 113 and 115, respectively. Further loss of Cl yields an m/e value of 78.

By use of 25 mL of water instead of 25 g of berries, mean recovery and standard deviation (three samples) of 25 μg of 6-CPA and 6-CPAmide as 6-CPA methyl ester were 78 ± 5 and 75 ± 3%, respectively. Direct reaction of 25 μg of 6-CPA analytical standard with BF_3–methanol gave an 87 ± 4% conversion (recovery).

Strawberry samples (25 g) fortified with 25, 12.5, and 2.5 μg of 6-CPAmide gave recoveries of 6-CPA methyl ester of 64 ± 3, 68 ± 2, and 67 ± 5%, respectively. Fortification with 25 μg of 6-CPA and 37 μg of nitrapyrin (equivalent to 25 μg of 6-CPA) gave recoveries of 6-CPA methyl ester of 67 ± 3 and 74 ± 2%, respectively.

Extraction of Soil. *Nitrapyrin.* A 25-g sample of sieved soil (2 mm) was extracted twice by using 50 mL of acetone each time with shaking 30 min on a reciprocating shaker. Each extract was successively gravity filtered through a No. 42 Whatman filter paper. The solvent from the combined extracts was removed in a rotary vacuum evaporator at 35 °C. The residue was dissolved in hexane for GLC analysis.

6-CPA. A 25-g sample was extracted twice by using 1 g of $Ca(OH)_2$ and 50 mL of water with 30-min shaking each time. The extract was vacuum filtered through a No. 1 Whatman filter paper in a Büchner funnel. To the combined filtrate, 4 mL of concentrated H_3PO_4 and 30 g of NaCl were added. The mixture was extracted twice by using 50 mL of ether and a 1-min shaking each time. The ether was removed and the residue was derivatized with BF_3–CH_3OH as described above for 6-CPA residues from strawberries.

Procedural Recovery. Mean recoveries and standard deviations for air-dried soil fortified at 2.0 and 0.1 ppm were 90 ± 2 and 94 ± 2%, respectively, for nitrapyrin (three samples) and 80 ± 5 and 77 ± 6%, respectively, for 6-CPA (six samples).

Effect of Frozen Storage on Residues. Strawberries were macerated and fortified with both 1.0 ppm of nitrapyrin and 0.5 ppm of 6-CPA, and 100-g subsamples were placed into individual plastic bags and frozen (−16 °C). Three replicate samples were analyzed after 1, 7, 22, 60, and 223 days of storage. Recoveries and standard deviations for nitrapyrin were 82 ± 4, 81 ± 3, 89 ± 6, 80 ± 3, and 69 ± 2%, respectively, and for 6-CPA were 81 ± 3, 82 ± 1, 81 ± 4, 83 ± 2, and 99 ± 10%, respectively. The 60-day samples indicated no adverse effects due to frozen storage for this storage interval; all field samples were therefore analyzed within 60 days after sample collection. The 223-day samples indicated a 0.14-ppm decrease in

nitrapyrin residues and a corresponding 0.18-ppm increase in 6-CPA residues.

Both air-dried and moist (60% saturation) Arlington fine sandy loam soil (2-mm sieved) were fortified with either 1.0 ppm of nitrapyrin or 6-CPA and frozen (−16 °C). Subsamples were analyzed after 2 days and after 4, 6, 14, 18, and 27 weeks of storage. For air-dried soil, mean recoveries and standard deviations (given only if three samples analyzed) were 82, 92 ± 2, 96 ± 3, 80 ± 3, 76 ± 2, and 67 ± 2%, respectively, for nitrapyrin and 63, 60 ± 7, 77 ± 2, 74 ± 5, 82 ± 4, and 71 ± 10%, respectively, for 6-CPA. For moist soil, mean recoveries and standard deviations (given only if three samples analyzed) were 75, 79, 83 ± 3, 61, 61 ± 3, and 86 ± 3%, respectively, for nitrapyrin and 72, 71 76 ± 2, 78 ± 3, 78 ± 5, and 89 ± 0%, respectively for 6-CPA. The overall data indicate possible loss of nitrapyrin after longer than 3-months frozen storage of air-dried soil. Residues of nitrapyrin in moist soil and 6-CPA in both air-dried soil and moist soil appeared stable under frozen storage up to 27 weeks. Field samples were analyzed within 2 weeks of sample collection.

Sampling. Strawberries were handpicked once a week. For each plot, a subsample consisting of one to three standard "baskets" was selected for residue analysis.

For each plot, a composite of five 2.5 × 15 cm soil core samples was taken between plants. The polyethylene cover was lifted and the core sampler was angled into the root zone. The core samples were mixed and a 50-g subsample was removed for residue analysis. Another subsample was removed for moisture determination.

Analysis. Samples were analyzed for nitrapyrin or methyl 6-chloropicolinate by gas chromatogrphy using a Hewlett-Packard nitrogen/phosphorus detector. A 1.2 m × 2 mm i.d. glass column packed with 5% Reoplex 400 on 60–80 mesh Gas-Chrom Q was used. Inlet, column, and detector temperatures were 250, 150, and 300 °C, respectively, with a nitrogen carrier gas flow rate of 30 mL/min.

At each of the four sampling dates, eight strawberry samples were analyzed: four treated samples (two cultivars, two fertilization rates) and four corresponding control samples. No corrections for recoveries as determined from fortified control samples were made.

Analytical standards of nitrapyrin, 6-CPA, and 6-CPA methyl ester were provided by the Dow Chemical Co., Midland, MI.

RESULTS AND DISCUSSION

Residue Data. *Strawberries.* Two main commercial varieties of strawberry cultivars, Tufts and Tioga, were each planted on Nov 2, 1978, in separate plots which, on the previous day, had received fertilizer treatments of 21–0–0 or 16–20–0, with and without added N-Serve at 0.5 lb of AI/acre.

Strawberry samples for residue analysis were collected on March 22, April 6 and 19, May 3, and June 14, 1979. Sample collection spanned the entire harvesting period for the "winter" planting. No determinable residues (≥0.04 ppm) of nitrapyrin were detected in any of the samples. Determinable residues (≥0.04 ppm) of 6-chloropicolinic acid, the nitrapyrin hydrolysis product, was found in only four samples from the 16–20–0 plus N-Serve plots. The April 6 and 19 samples from the Tufts plot contained 0.04 ppm and the March 22 and April 19 samples from the Tioga plots contained 0.09 and 0.08 ppm, respectively. These results were confirmed by the acid digestion procedure wherein samples were refluxed for 2 h with 6 N HCl solution to obtain total 6-CPA residues (any 6-CPA conjugates would have been hydrolyzed to 6-CPA). Determinable total 6-CPA residues (≥0.02 ppm) were found in seven samples. For the 20–0–0 plus N-Serve treated plots, the April 19 Tufts and March 22 Tioga samples contained 0.02 ppm. For the 16–20–0 plus N-Serve treated plots, the March 22 and April 6 and 19 Tufts samples contained 0.03, 0.04, and 0.03 ppm, respectively. The March 22 and April 19 Tioga samples contained 0.07 and 0.05 ppm, respectively. Figures 1, 2, and 3 give sample chromatograms for the analysis of strawberries for nitrapyrin, 6-CPA, and total 6-CPA, respectively.

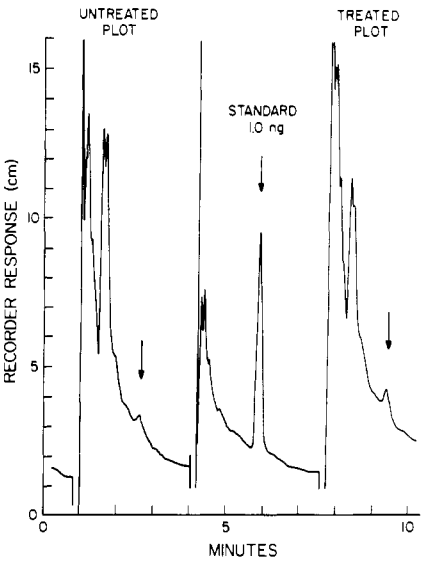

Figure 1. Sample chromatograms of extracts prepared from strawberries harvested April 19, 1979, and analyzed for nitrapyrin. The strawberries were collected from untreated (16–20–0 fertilizer only) and treated (16–20–0 fertilizer plus N-Serve) plots. Chromatograms represent injection of extractives from 15 mg of untreated and 12 mg of treated berries which contained <0.04 ppm of nitrapyrin; arrows indicate the position of the nitrapyrin peak. Standard represents 1.0 ng of nitrapyrin.

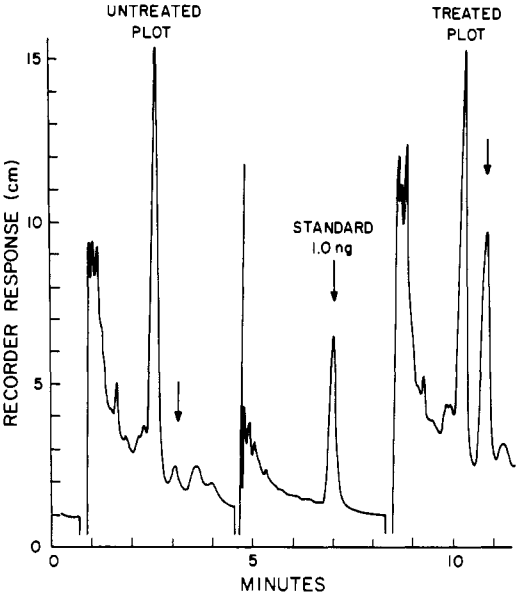

Figure 2. Sample chromatograms of extracts prepared from strawberries harvested April 19, 1979, and analyzed for 6-CPA as its methyl ester. The strawberries were collected from untreated (16–20–0 fertilizer only) and treated (16–20–0 fertilizer plus N-Serve) plots. Chromatograms represent injection of extractives from 18 mg of untreated and 19 mg of treated berries which contained <0.04 and 0.07 ppm of 6-CPA, respectively; arrows indicate the position of the 6-CPA methyl ester peak. Standard represents 1.0 ng of 6-CPA as its methyl ester.

Redemann et al. (1965) demonstrated that corn, lettuce, tomatoes, oats, and carrots planted in soil treated with

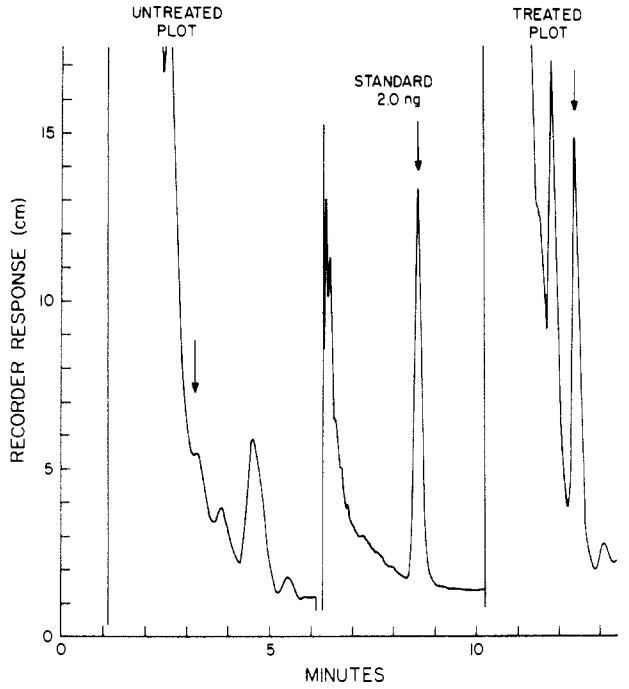

Figure 3. Sample chromatogram of extracts prepared from strawberries harvested April 19, 1979, and analyzed after acid hydrolysis for 6-CPA as its methyl ester. The strawberries were collected from untreated (16–20–0 fertilizer only) and treated (16–20–0 fertilizer plus N-Serve) plots. Chromatograms represent injection of extractives from 31 mg of untreated and 37 mg of treated berries which contained <0.02 and 0.05 ppm of 6-CPA, respectively; arrows indicate the position of the 6-CPA methyl ester peak. Standard represents 2.0 ng of 6-CPA as its methyl ester.

[^{14}C]nitrapyrin contained radioactive residues in most of their organs. Paper chromatography of extracts of oat seeds and corn, lettuce, and tomato leaves demonstrated that the principal residue present was 6-CPA rather than the parent compound. The absence of determinable residues (≥0.04 ppm) of nitrapyrin and the low levels of 6-CPA reported here for strawberry fruit are consistent with these results. These authors proposed that much of the residue in the plant consisted of 6-CPA which was formed in the soil by hydrolysis of nitrapyrin. Meikle et al. (1978) reported 6-CPA to be the only hydrolysis product of nitrapyrin in buffered distilled water. The hydrolysis rate for nitrapyrin was independent of pH over the range 3.2–8.4. Meikle and Redemann (1966) reported that 6-CPA is taken up by the corn plant from soil. Using radiolabeled 6-CPA, it was demonstrated that a small portion was converted to 2-chloropyridine, some was esterified, and a small part, the authors suggested, was conjugated with insoluble protein. In addition, some of the 6-CPA and/or its subsequent metabolites were reportedly dehalogenated to yield chloride ion. They suggested that since the quantity of 6-CPA appearing as lipid and protein conjugates is substantial, any scheme for residue determination should take this into account by including a hydrolysis step. This suggestion was adopted for the present study; however, the procedures with and without the hydrolysis step gave essentially identical results in our hands.

Soil. Soil samples were collected on March 12, April 11, May 11, and June 13, 1979. The first sample was obtained 131 days after soil application of N-Serve on Nov 1, 1978. No determinable residues of nitrapyrin (≥0.04 ppm) or 6-CPA (>0.02 ppm) were found in the control plots. Mean nitrapyrin residues in the 15-cm core samples for the four treated plots were 0.30 ± 0.12, 0.18 ± 0.09, 0.11 ± 0.05 and 0.06 ± 0.04 ppm (air-dry basis), respectively, for the four sampling dates. These data fit the line ln (residue, ppm) = −0.017(time) + ln 2.9 (Nov 1, 1978, taken as 0 day); the correlation coefficient was 0.99 and the half-life was 41 days. The mean 6-CPA residue values in the 15-cm core samples were 0.16 ± 0.06, 0.08 ± 0.01, 0.12 ± 0.05, and 0.07 ± 0.03 ppm (air-dry basis), respectively, and did not fit any pattern tried.

Table I. Strawberry Yield Data

year	treatment[c]	g/ plant	tons/ acre	mean fruit size, g
1977-1978[a]	none	316	13.6	15.8
	21-0-0	652	28.2	19.5
	21-0-0 + N-Serve	703	30.5	19.0
	16-20-0	723	31.2	19.1
	16-20-0 + N-Serve	767	33.2	19.1
	urea 46-0-0	522	22.5	16.8
	urea 46-0-0 + N-Serve	597	25.8	17.9
1978-1979[b]	none	169	7.3	13.6
	21-0-0	541	23.3	17.1
	21-0-0 + N-Serve	630	27.2	17.8
	16-20-0	642	27.7	17.1
	16-20-0 + N-Serve	670	29.4	18.2

[a] Selection of Tufts, C51, C34, and C55 strawberry varieties planted Nov 1, 1977, in Orange County. [b] Tufts and Tioga strawberry varieties planted Nov 2, 1978, in Orange County. [c] Nitrogen rate used was 200 lb/acre. N-Serve was used at 1 qt of 24E formulation/acre (0.5 lb of AI/acre). The symbolism 21-0-0, for example, represents fertilizer composition as percent nitrogen, phosphorus, and potassium, respectively.

Redemann et al. (1964) reported that nitrapyrin added to a California sandy loam soil of low organic matter (0.3%) dissipated by first-order kinetics with a half-life of 22 days when the soil was moistened to field capacity, placed in covered jars, and kept at 22 °C. They demonstrated that the rate of loss of nitrapyrin varied from soil to soil and that volatilization was important in nitrapyrin dissipation. After 1 year, 6-CPA was the sole product recoverable from soil fortified with radiolabeled nitrapyrin. Herlihy and Quirke (1975) also reported that nitrapyrin dissipated by first-order kinetics from soil moistened to field capacity; they demonstrated that nitrapyrin persisted longer in soil maintained at 10 °C than at 20 °C.

Efficacy Data. Table I gives the strawberry yield data for crops planted in Nov of 1977 and 1978. Table II gives the results of the analysis of variance applied to the data of Table I. The use of nitrogen fertilizer increased crop yield; data were significant at the 0.1% level. The use of nonurea nitrogen-containing fertilizers was more effective; data were significant at the 0.1% level. The use of 16–20–0 fertilizer was preferred over the 21–0–0 fertilizer; data were significant at the 5% level. The use of N-Serve in combination with nitrogen-containing fertilizer increased yield; data were signigicant at the 5% level for the 1977–1978 winter planting and at the 10% level for the 1978–1979 winter planting. These results are in agreement with those of Welch et al. (1979), who reported that addition of nitrapyrin resulted in a significant (5% level) yield increase over that of ammonium sulfate alone applied at rates of 75 and 150 lb of nitrogen/acre. The increase of 2.5 and 2.8 tons/acre for the 1977–1978 and 1978–1979 plantings, respectively, represents a sizable return to the grower as strawberries are a high cash value crop.

Table II. Analysis of Variance of Strawberry Yield Data in Table I

treatment	yield, tons/acre 1977-1978	1978-1979	both years
none	13.7	7.3	11.5
fertilizer	28.6	26.9	29.5
significant at	0.1%	0.1%	0.1%
urea	24.2		
other nitrogen	30.8		
significant at	0.1%		
21-0-0	29.3	25.3	28.0
16-20-0	32.2	28.6	31.0
significant at	5%	5%	1%
no N-Serve	27.3	25.5	28.3
N-Serve	29.8	28.3	30.6
significant at	5%	10%	5%

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Movement of Cypermethrin, Decamethrin, Permethrin, and Their Degradation Products in Soil

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The movement of the synthetic pyrethroid insecticides decamethrin, cis and trans isomers of cypermethrin, and cis and trans isomers of permethrin and their degradation products DCVA [*cis,trans*-3-(2,3-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate], PBAl (3-phenoxybenzyl alcohol), and PBAc (3-phenoxybenzoic acid) was examined in a Hagerstown silty clay, silty clay loam, and a Tifton loamy sand. Movement in both soil columns and soil thin-layer chromatographic (TLC) systems was compared. Decamethrin, *cis*- and *trans*-cypermethrin, and *cis*- and *trans*-permethrin were immobile in all soils. PBAl was only slightly mobile in each of the three soils examined. Both DCVA and PBAc were mobile in each of the three soils examined, and the separation of the cis and trans isomers of DCVA was observed in some soils. Both DCVA and PBAc were less mobile in acid soils than in an alkaline soil. Soil TLC provided an exceptionally comparable picture of soil movement of the compounds examined when compared with the unsaturated soil columns.

The new synthetic pyrethroid insecticides have great potential as agricultural insecticides, because of their high insecticidal activity, low mammalian toxicity, and adequate stability in air and light (Elliott et al., 1973). Although a considerable amount of information is available about their metabolism in plants and animals, only a limited amount has been published which describes their degradation and movement in soils.

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Kaufman et al. (1977) initially described the degradation of permethrin in soil. That investigation indicated that permethrin [(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] was rapidly degraded in soil and that soil microorganisms played a significant role in permethrin degradation. The principal mechanism of degradation of permethrin involves hydrolysis to 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylic acid (DCVA) and 3-phenoxybenzyl alcohol (PBAl). Further metabolism of both products was demonstrated by the measurement of the ^{14}C labels as $^{14}CO_2$. Similar results have been described by other investigators with cypermethrin [cyano-(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate] (Roberts and Standen, 1977a), fen-