Persistence and Uptake of Carbofuran in a Humic Mesisol and the Effects of Drying and Storing Soil Samples on Residue Levels

Roy Greenhalgh* and Andre Belanger

Four extraction procedures were evaluated for the recovery of carbofuran and 3-keto- and 3-hydroxy-carbofuran from a fortified humic mesisol and a sandy loam soil. Aqueous HCl gave the lowest levels of coextractants, which interfered with quantitation of the intact compounds by a GC thermionic detector. Carbofuran was applied to a humic mesisol at 2.24 and 4.48 kg of a.i./ha in the field; the half-life of carbofuran was 15–38 days whether applied broadcast or banded. Both 3-hydroxycarbofuran and 3-ketocarbofuran were detected as transformation products, the former reaching maximum levels between days 1 and 7 and the latter between days 16 and 36. After 30 days, the carbofuran levels in soil previously treated with the insecticide were appreciably less than those treated for the first time. This was attributed to different induction times for the growth of carbofuran-degrading microorganisms in the soils. Carbofuran was taken up from the humic mesisol by crops; the levels were highest in onions and then lettuce and carrots for the banded application. Drying the soil samples at room temperature, 48 h in the dark, resulted in a decrease of residues in the order carbofuran < 3-hydroxycarbofuran < 3-keto-carbofuran. Storage of both moist (150–180% water) and dried samples (9–11% water) for 6 months at −20 °C resulted in further reduction, especially for the moist samples. Under both storage and drying conditions, the order of loss is reflected in the chemical stability of the three compounds. It is postulated that degradation on cold storage resulted from soil enzyme activity.

Carbofuran has been used extensively in agriculture over the past decade both as a systemic insecticide and as a nematocide. As a result, a considerable amount of data has been accumulated concerned with residue levels, analytical methodology, metabolism, and toxicology ("Initial Scientific and Minieconomic Review of Carbofuran", 1976; JMPR monograph, 1976; "Carbofuran, Criteria for Interpreting the Effects of Its Use on Environmental Quality", 1979), and its degradation in soils (Laveglia and Dahm, 1977). However, data related to the use of carbofuran in organic soils, recently summarized by Miles and Harris (1978), is quite limited.

Soil organic matter adsorbs pesticides and is considered to be an environmental factor, which together with the chemical properties of the pesticide will influence the persistence, bioavailability, and rate of degradation (Jamet and Piedallu, 1975). Thus, Getzin (1973) observed that carbofuran degraded more slowly in a muck soil (40% organic matter) than in a silt or clay loam soils. Carbofuran residues have also been found to accumulate in a clay muck soil, to the extent that residue levels of 3.8 ppm were found after two successive annual treatments (Williams et al., 1976a). In a survey of 22 farms with a history of carbofuran use, 19 out of 22 organic soils analyzed were found to have residues > 0.04 ppm (Miles and Harris, 1979). The highest total carbamate residue level was 1.5 ppm, of which 0.3 ppm was 3-ketocarbofuran. The same authors (Miles and Harris, 1978) also reported that one soil sampled late in the crop season contained 8.7 ppm of total carbamate.

The object of the present study was to obtain more data on the persistence and crop uptake of carbofuran applied to an organic soil (82% organic matter) at recommended rates. In addition, the effects of drying and storing of soil samples on the residues of carbofuran and 3-keto- and 3-hydroxycarbofuran were studied.

Chemistry and Biology Research Institute, Agriculture Canada, Ottawa, Ontario K1A 0C6, Canada (R.G.), and Research Station, Agriculture Canada, Saint Jean, Québec J3B 6Z8, Canada (A.B.).

EXPERIMENTAL SECTION

Field Plots. The field trails were conducted at Ste. Clothide, P.Q. The soil is a humic mesisol, pH 5.6–5.8, containing 43% carbon, 2.5% nitrogen, and 18% mineral matter. It has a cation-exchange capacity of 163 mequiv/100 g, a bulk density of 0.35, and a field moisture capacity of 200% of dry weight. Individual plots (3.6 × 6 m) were divided into three subplots (3.6 × 2 m). Eight rows of crops, i.e., Imperial lettuce, Autumn Spice onions, and Gold Pak carrots, were planted in each plot. Carbofuran (10G formulation) was applied at the rates 2.24 and 4.48 kg of a.i./ha as a band and a broadcast application.

Field Sampling. *Soil.* Samples from field plots were collected before treatment and after 1, 15, 30, 60, and 120 days. Composite samples were taken from each subplot by combining six random soil cores (10 cm deep × 15 cm diameter) for a total of 18 cores/plot. In banded plots, the cores were taken within the band. After the samples were mixed 0.5-kg subsamples were taken from each composited subplot and stored in plastic bags at −20 °C until analyzed. Samples were sieved and representative samples (20 g) analyzed.

Crops. Thirty random samples were collected from each subplot and rinsed with cold water. Onions and lettuce heads were halved, and one part was retained for analysis. Samples from each subplot were processed and analyzed separately.

Analytical Method. Both crop (50 g) and soil (20 g) samples were extracted by refluxing with 0.25 N aqueous HCl (Cook, 1973), followed by cleanup on acid alumina (Williams et al., 1976a). Initially, the 2,4-dinitrophenyl derivative of carbofuran was used for analysis and quantitated by a GC electron capture detector (ECD). Later, intact carbofuran and 3-keto- and 3-hydroxycarbofuran were quantitated by using a GC with a heated bead thermionic detector. The recovery from crop samples fortified at 0.02 ppm of carbofuran were 94 and 95% for carrots and lettuce, respectively, and 90% for onions, fortified at the 0.05-ppm level.

Gas Chromatography. A Pye Model 104 gas chromatograph equipped with a ^{63}Ni ECD and a Perkin-Elmer NP detector was used. The 2,4-dinitrophenyl ethers were
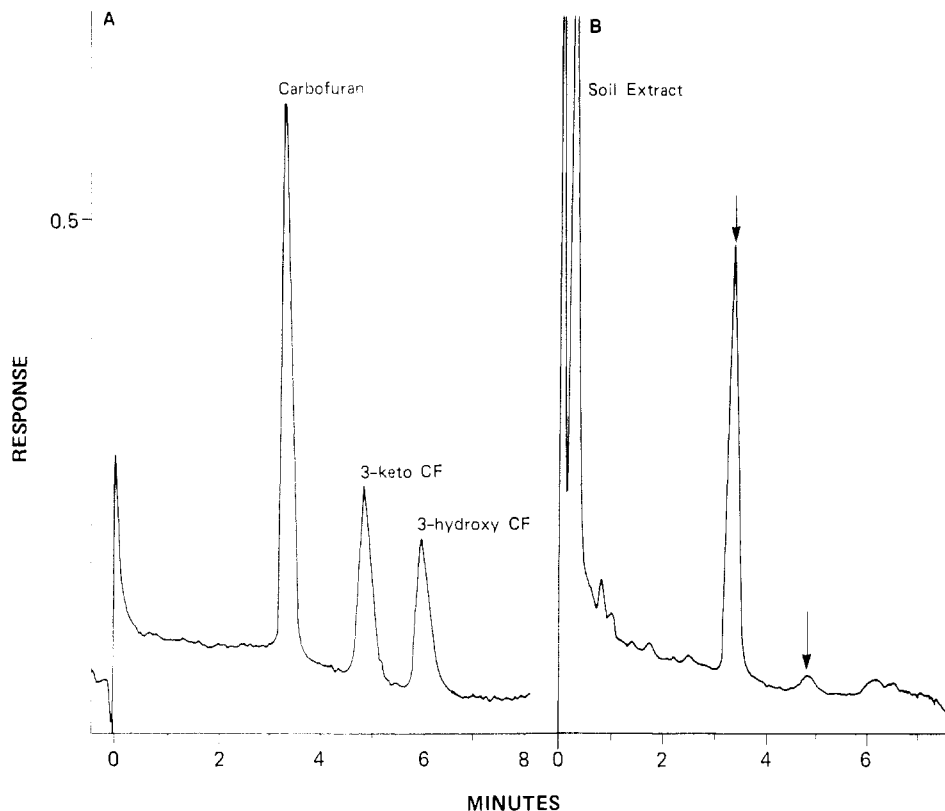
Figure 1. Analysis of carbofuran and 3-keto- and 3-hydroxycarbofuran in the cleaned up extract of field-treated humic mesisol using an NP thermionic detector. (A) Standards: carbofuran (8 ng); 3-ketocarbofuran (5 ng); 3-hydroxycarbofuran (5 ng). (B) Cleaned up soil extract, showing the presence of carbofuran and the 3-keto analogue. GC conditions: column 1.8 × 4 mm i.d., 4% SE-30/6% QF-1 on Gas-Chrom Q; column temperature, 205 °C; column flow rate, 30 mL/min helium; detector flows rates, 100 mL/min air and 2 mL/min hydrogen; standing current, 3 pA.

Table I. Extraction Efficiency of Various Procedures for Carbofuran and 3-Keto- and 3-Hydroxycarbofuran from a Humic Mesisol and a Sandy Loam Soil[a, b]

	recovery, %[c]					
	carbofuran		3-ketocarbofuran		3-hydroxycarbofuran	
extraction solvent	HM	SL	HM	SL	HM	SL
aqueous acidic NH_4Ac	82	91	95	101	64	94
aqueous HCl	85	90	81	84	67	78
CH_2Cl_2-MeOH	78	84	82	87	61	72
CH_3CN	80	86	78	84	62	76

[a] Soil fortified at 0.05 ppm for each compound.   [b] Average of duplicate extractions.   [c] HM = humic mesisol; SL = sandy loam.

chromatographed on a 1 m × 4 mm i.d. glass column packed with 80–100-mesh Gas-Chrom Q coated with 3% OV-17. The operating conditions were as follows: column temperature, 230 °C; detector temperature, 270 °C; carrier gas, 60 mL/min nitrogen. Intact carbofuran and 3-keto- and 3-hydroxycarbofuran were separated by using a 1.8 m × 4 mm i.d. glass column packed with 100–120-mesh Gas-Chrom Q coated with 4% SE-30/6% QF-1. The chromatographic conditions were as follows: column temperature, 205 °C; detector temperature, 210 °C; carrier gas, 30 mL/min helium; detector gas flow rates, 100 mL/min air and 2 mL/min hydrogen; standing current, 3 pA.

RESULTS AND DISCUSSION

Analytical procedures for carbofuran and its metabolites in various matrices have been reviewed ("Carbofuran, Criteria for Interpreting the Effects of Its Use on Environmental Quality", 1979). Derivatization was often involved in earlier procedures, as a means of increasing both thermal stability and sensitivity of the carbamate moiety. Today, the use of selective GC nitrogen detectors (ther-

mionic) is preferred for the analysis of carbamates (Ahmad et al., 1979). They are sensitive enough to quantitate intact residues of carbofuran and 3-keto- and 3-hydroxycarbofuran (Figure 1). For a signal/noise level of 2:1, the minimum detectable amounts are 2.0, 2.9, and 4.4 × 10⁻¹¹ g/s, respectively, for the three compounds with the Perkin-Elmer NP detector.

The extraction efficiency of four procedures for determining intact carbofuran and its transformation products, 3-keto- and 3-hydroxycarbofuran, in the humic mesisol were determined and compared with that from a sandy loam. The latter with a low organic content (1.2%) should give extracts low in coextractants and reduced binding. One procedure involves refluxing with aqueous HCl (Cook, 1973), while in other procedures tested the samples were shaken with aqueous acidic ammonum acetate (Caro et al., 1973b), CH_2Cl_2–CH_3OH (Williams et al., 1976b), and acetonitrile. A standard cleanup procedure on acidic alumina was employed and quantitation was by a GC thermionic detector. The recovery data are shown in Table I.

Table II. Residues of Carbofuran in Onions, Lettuce, and Carrots Grown in Humic Mesisol Treated with 10G Formulation, Broadcast and Banded

application rate, kg of a.i./ha	residue levels,[a] ppm					
	onions		lettuce		carrots	
	band	broadcast	band	broadcast	band	broadcast
2.24	0.09	<0.05	0.05	<0.02	0.3	<0.02
4.48	0.14	0.06	0.08	0.02	0.7	<0.02
control		<0.05		<0.02		<0.02

[a] Average values for duplicate analyses of three subplot composite samples.

Table III. Residue Levels of Carbofuran in Humic Mesisol Field Treated at Different Rates

rate, kg of a.i./ha	residue level, ppm[a]						
	control	day 1	day 15	day 30	day 60	day 120	year
band							
8.96	–	83.52	–	37.41	–	0.47	1974
4.48	0.03	36.50	–	20.72	–	0.41	1974
	0.02	36.19	–	14.21	–	0.81	1974
	0.10	39.96	19.47	2.50	1.02	0.36	1975[b]
	0.12	28.62	14.61	1.01	0.96	0.39	1975[b]
	0.04	34.05	23.89	19.23	8.23	0.52	1976
2.24	0.09	12.21	9.54	2.39	0.77	0.12	1975[b]
	0.14	10.12	9.07	1.42	0.63	0.10	1975[b]
	0.02	9.28	9.15	4.80	2.19	0.48	1976
broadcast							
4.48	0.03	3.23	–	1.43	–	0.35	1974
	0.09	6.72	3.09	1.65	0.89	0.66	1975[b]
2.24	0.02	1.82	–	0.85	–	0.19	1974
	0.10	2.54	2.23	0.73	0.56	0.42	1975[b]

[a] Levels reported are the average of duplicate analyses of three subplot composite samples. [b] Retreated plots.

Higher recoveries were obtained from the fortified sandy loam soil than from the humic mesisol, especially with 3-hydroxycarbofuran. The soil extracts obtained with both organic solvents contained coextractants, which interfered with quantitation by the GC thermionic detector, and for this reason, aqueous HCl was preferred as an extraction solvent.

The residue levels in crops grown in the field plots are shown in Table II. As expected, crop residues are highest in the banded plots with the levels in onions being the highest, followed by lettuce and carrots.

Freshly exposed organic soil was treated with 10G carbofuran granular formulation and retreated the following year. Residue data for carbofuran with respect to time are shown in Table III. Levels in the control samples (day 0) of soil treated for the first time and retreated soil indicated a small, but significant difference between the means, 0.027 and 0.106 ppm, respectively. The low levels in the retreated soil, that is, after wintering over, are consistent with the carbofuran levels (0.09–1.2 ppm) that Miles and Harris (1979) found prewinter in a similar organic soil. The observed half-life for carbofuran in these field-trials ranged from 15 to 38 days. Other persistence studies reported half-lifes of 46–117 days in a peat soil (Caro et al., 1973a) and 21–350 days for carbofuran in a silt loam soil (Getzin, 1973).

The persistence of carbofuran in soils will depend on factors such as the soil type, method of application (Ahmad et al., 1979), level and nature of soil microbial activity (Williams et al., 1976b), and pH (Getzin, 1973), as well as environmental factors, such as temperature and soil air/water ratio. However, the chemical degradation of carbofuran in neutral and acid soils is relatively slow, suggesting that purely chemical processes are not responsible for the rapid degradation of carbofuran observed in these field trials. Carbofuran is known to undergo microbial degradation in soils in both anaerobic (Venkateswarlu et

al., 1977) and aerobic conditions (Getzin, 1973), with actinomycetes being particularly effective (Williams et al., 1976b). In the current study, it was observed that both band and broadcast applications of carbofuran to the humic mesisol increased the number of soil bacteria plus actinomycetes, up to 4-fold within 33 days. In addition, there was a 40% increase in the CO_2 evolved from the treated soil after 48 days (Mathur et al., 1976). These results suggest greater microbial activity occurred in the treated plots than in the control, which resulted in the rapid degradation of carbofuran in this soil. This factor may also explain that, by day 30, the residue levels in the retreated plots are distinctly less than those in plots treated for the first time (Table III). The induction period, during which proliferation of microorganisms capable of decomposing carbofuran occurs, would be expected to be shorter in retreated plots than in those treated for the first time, because of their harboring these specific microorganisms. Further substance is given to this idea by the recent work of Venkateswarlu et al. (1980), who showed that a bacterium isolated from a carbofuran-amended soil enhanced the degradation of carbaryl. Siddaramappa et al. (1979) also observed the same phenomena with carbofuran in anaerobic soils.

Drying and storage generally result in a decline of any pesticide residues present (Swain, 1979). This phenomena has also been observed with carbofuran (Williams et al., 1976b). To study this effect in humic mesisol, we treated soil not previously exposed to the pesticide with 4.56 kg of a.i./ha 10G carbofuran formulation by band application. Soil samples were analyzed as received (moisture content 150–180% dry weight basis) after air drying in the dark at room temperature for 48 h (9–11% moisture) and again after storage of both sets of samples in plastic bags at –20 °C for 6 months. The residue levels of carbofuran and 3-keto- and 3-hydroxycarbofuran found are given in Table IV. The half-life of carbofuran observed in this experi-

Table IV. Residue Levels of Carbofuran and 3-Keto- and 3-Hydroxycarbofuran in Field-Treated Humic Mesisol (4.48 kg/ha 10G) before and after Drying and after Storage

| | day 1 | | day 7 | | day 16 | | day 36 | | day 69 | | day 11 | | day 119 | |
compound	moist	dry	moist	dry	moist	dry	moist	dry	moist	dry	moist	dry	moist	dry
drying[b]														
carbofuran	34.1	33.7	29.5	27.1	23.9	22.9	19.2	13.4	8.2	5.4	0.5	0.5	0.05	0.5
3-ketocarbofuran	0.36	0.21	0.4	0.3	0.6	0.4	0.5	0.4	0.3	0.4	0.1	0.1	0.1	0.1
3-hydroxycarbofuran	0.70	0.28	0.62	0.17	0.11	0.10	0.14	0.10	0.11	0.08	0.07	0.5	0.07	0.05
storage[c]														
carbofuran	25.9	21.8	25.5	22.1	20.9	19.6	12.2	12.5	4.1	5.3	0.3	0.5	0.3	0.5
3-ketocarbofuran	0.12	0.16	0.28	0.28	0.30	0.21	0.35	0.36	0.2	–	0.05	0.1	0.05	0.1
3-hydroxycarbofuran	–	–	–	–	–	–	–	–	–		–	–	–	–

[a] Levels reported are the average of duplicate analyses of three subplot composite samples. [b] Moist soil samples were dried at room temperature in the dark for 48 h. [c] Moist and dried soil samples were stored at –20 °C for 6 months.

ment was 40 days, which is of the same order as that found in the earlier results.

Both 3-ketocarbofuran and 3-hydroxycarbofuran were detected as metabolites; whereas the former has been frequently observed in aerobic soils, the latter has only been sporadically reported (Getzin, 1973) and then mostly under anaerobic conditions (Venkateswarlu and Sethunathan, 1978). The concentration/time profile for 3-ketocarbofuran reaches a maximum within 16 days and then slowly declines (Table IV). By contrast, the concentration of 3-hydroxycarbofuran was at a maximum before 7 days and then declined rapidly. The possibility that the 3-hydroxycarbofuran was present in the granular formulation used, as Archer (1976) found in a flowable formulation, was discounted by analysis. This indicates 3-hydroxycarbofuran was a degradation product and not an impurity. Thirumurthi et al. (1975) also observed its presence in an aerobic soil at levels in excess of those of 3-ketocarbofuran. It was not, however, very stable, reaching maximum level by 20 days and then disappearing rapidly by hydrolysis to the phenol and conversion to 3-ketocarbofuran.

The average losses of carbofuran, 3-keto- and 3-hydroxycarbofuran residues on drying the soil samples were 18 ± 12, 21 ± 5, and 35 ± 10%, respectively. When the moist soil samples were stored at –20 °C for 6 months, the average losses for the three compounds were 28 ± 15, 43 ± 23, and 100% and in dried samples 14 ± 12, 25 ± 12, and 100% respectively. Both in the drying and storage processes the order in which losses occurred, i.e., 3-hydroxy > 3-keto > carbofuran, reflects their chemical stability. In all cases, the losses were greater for soil samples stored in a moist condition. William et al. (1976b) also observed the losses of carbofuran and 3-hydroxycarbon residues in fortified loam soils stored at –16 °C.

The cause of the loss of insecticide residues during low-temperature storage was not identified. It could result from increased binding, either chemical, microbial, or enzymatic reactions, although at –20 °C both chemical and microbial hydrolysis would be expected to be negligible. Tabatabai and Bremner (1970) showed that soil enzyme activity survived freezing. Subsequently, it was shown that the hydrolytic activities of urease, phosphatase, and sulfatase continued at temperatures as low as –20 °C but not –30 °C (Bremner and Zantua, 1975). This activity was attributed to enzyme–substrate interaction in unfrozen water at the surface of soil particles. The enzymatic activity observed on incubation soils at subzero temperatures was due to enzymes present in the soil before incubation and not those produced during the cold storage when no microbial activity occurs. Based on this evidence, it is suggested that residues of carbofuran and its two oxidation

products in soil at –20 °C are degraded enzymatically rather than by microorganisms or chemically in unfrozen water films in soil. However, other factors such as the possible increase in absorption due to freezing and drying may also contribute.

In summary, it appears that the disappearance of carbofuran coincided with high microbial activity in the treated soils, suggesting that soil organisms contribute to the rapid degradation of carbofuran observed in organic soils. The faster decomposition of carbofuran applied for the second time supports this conclusion, suggesting the presence of a population readily adaptable to or already induced for degrading the carbamate. In contrast, the loss of carbofuran and 3-keto- and 3-hydroxycarbofuran residues in soil samples stored in –20 °C is thought to be due to enzymatic degradation.

LITERATURE CITED

Ahmad, N.; Walgenback, D. D.; Sutter, G. R. Bull. Environ. Contam. Toxicol. 1979, 23, 572–574.
Archer, T. E. J. Agric. Food Chem. 1976, 24, 1057–1062.
Bremner, J. M.; Zantua, M. I. Soil Biol. Biochem. 1975, 7, 383–387.
"Carbofuran, Criteria for Interpreting the Effects of Its Use on Environmental Quality". Environmental Secretariat, N.R.C. Ottawa, 1979, NRCC No. 16740.
Caro, J. H.; Glotfelty, D. E.; Freeman, H. P.; Taylor, A. W. J. Assoc. Off. Anal. Chem. 1973, 56, 1319–1324.
Caro, J. H.; Freeman, H. P.; Glotfelty, D. W.; Turner, B. C.; Edwards, N. M. J. Agric. Food Chem. 1973, 21, 1010–1015.
Cook, R. F. Anal. Methods Pestic. Plant Growth Regul. 1973, 7, 187–210.
Getzin, L. W. Environ. Entomol. 1973, 2, 461–467.
"Initial Scientific and Minieconomic Review of Carbofuran". U.S. Environmental Protection Agency, Criteria and Evaluation Division, Washington, DC, July 1976, EPA 540/1-009.
Jamet, P.; Piedallu, M. A. Phytiatr.-Phytopharm. 1975, 24, 279–296.
JMPR monograph on the 1976 evaluations of some pesticide residues in food, carbofuran, FAO, Rome, 1976, AGP 1976/M/14, pp 135–186.
Laveglia, J.; Dahm, P. A. Annu. Rev. Entomol. 1977, 22, 483–513.
Mathur, S. P.; Hamilton, H. A.; Greenhalgh, R.; MacMillan, K. A.; Khan, S. U. Can. J. Soil Sci. 1976, 56, 89–96.
Miles, J. R. W.; Harris, C. R. J. Environ. Sci. Health, Part B 1978, B13, 199–209.
Miles, J. R. W.; Harris, C. R. J. Environ. Sci. Health, Part B 1979, B14, 655–661.
Siddaramappa, R.; Tiroc, A.; Watanabe, I. Nippon Noyaku Gakkaishi 1979, 4, 473–479.
Swain, D. J. J. Agric. Food Chem. 1979, 27, 915–916.
Tabatabai, M. A.; Bremner, J. M. Soil Sci. Soc. Am. Proc. 1970, 34, 427–429.

Thirumurthi, S.; Palaniswamy, P.; Subramanum, T. R. *Indian J. Agric. Chem.* **1975**, *8*, 211–215.

Venkateswarlu, K.; Chendrayon, K.; Sethunathan, N. *J. Environ. Sci. Health, Part B* **1980**, *B15*, 282–287.

Venkateswarlu, K.; Sethunathan, N. *J. Agric. Food Chem.* **1978**, *26*, 1148–1151.

Venkateswarlu, K.; Siddarame Gorda, T. K.; Sethunathan, N. *J. Agric. Food Chem.* **1977**, *25*, 533–537.

Williams, I. H.; Brown, M. J.; Whitehead, P. *Bull. Environ. Contam. Toxicol.* **1976a**, *15*, 242–244.

Williams, I. H.; Pepin, H. S.; Brown, M. J. *Bull. Environ. Contam. Toxicol.* **1976b**, *15*, 244–249.

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

Yutaka Iwata,* Travis M. Dinoff, J. Blair Bailey, Victor Voth,[1] and Francis A. Gunther

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

Department of Entomology, University of California, Riverside, California 92521.

[1]Present address: Pomology, University of California, South Coast Field Station, Santa Ana, CA 92705.