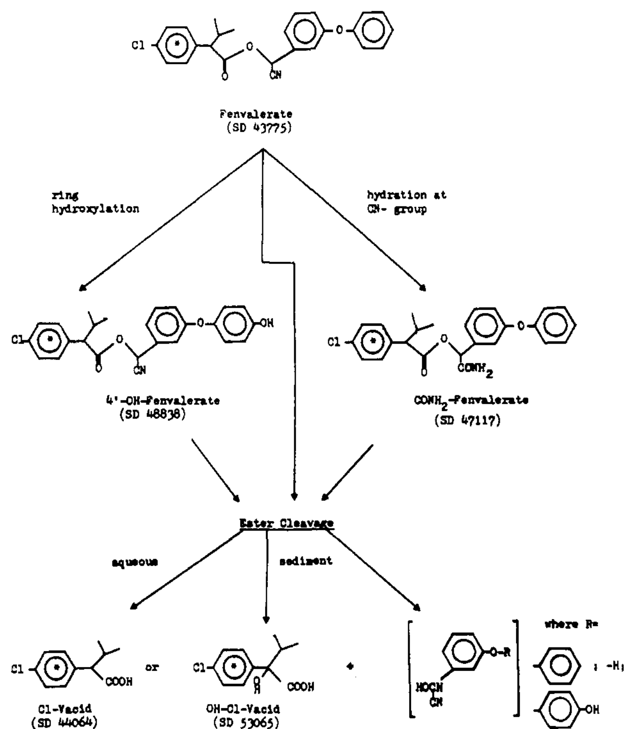


**Figure 7.** Proposed degradation pathway for fenvalerate in tidal marsh sediment.

fenvalerate (to form $CONH_2$-fenvalerate) was the predominant reaction on soil surfaces. Additional photodegradation reactions occurred via oxidation, decarboxylation, cleavage of ester or diphenyl ether linkages, and hydrolysis from $CONH_2$-fenvalerate to COOH-fenvalerate.

It is impossible to determine the exact mechansim(s) (i.e., microbial, hydrolytic, and photolytic) responsible for degrading fenvalerate in our study since no sterile or dark controls were run. However, it seems likely that fenvalerate was primarily degraded via microbial metabolism and/or hydrolysis rather than by photolysis. The reason for this is that the compound was uniformly applied to the sediment at the initiation of the study; therefore, only a small portion of the compound was exposed to light (via surface).

In this study, fairly good reproducibility (±10%) among replicate ecosystem tanks was shown in regards to physical measurements, plate counts, radiocarbon recovery, and quantitative and qualitative degradation patterns.

**Registry No.** Fenvalerate, 51630-58-1; OH-Cl-Vacid, 88036-36-6; $CONH_2$-fenvalerate, 67685-93-2; 4′-OH-fenvalerate, 67882-25-1.

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# COMMUNICATIONS

## Determination of Allidochlor Residues in Pre- and/or Postemergence-Treated Leeks

An analytical method for the gas chromatographic determination of the herbicide allidochlor (2-chloro-*N*,*N*-diallylacetamide) in leeks (*Allium porrum* L.) has been developed using a nitrogen-specific flame ionization detector. The limit of detection of the analytical method was 100 ppb based on a 5 g fresh-weight equivalent, with recoveries being in the order of 75% at the 100-ppb fortification level. Allidochlor residues in mature leeks were less than 100 ppb following either a 7.0 kg/ha preemergence application or a 7.0 kg/ha preemergence plus one or two 7.0 kg/ha postemergence applications.

Currently, allidochlor (2-chloro-*N*,*N*-diallylacetamide) is solely registered in Canada for use on onions with both preemergence and/or postemergence applications at 6.75 kg/ha being used to control annual grasses and broad-leaved weeds. Leeks, an onion-like crop, are grown on a limited hectarage in Eastern Canada, with the major

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hectarage being in the province of Quebec. Although allidochlor has shown potential for weed control in leeks (*Allium porrum* L.) (Dion, 1979, 1980), registration has not been granted since residue data were not available.

This paper describes a sensitive gas chromatrographic method for the analysis of allidochlor residues in leeks. On the basis of a previously published method ("Pesticide Analytical Manual", 1973), allidochlor was detected by using a nitrogen-specific flame ionization detector. The method was used to determine allidochlor residues in leeks that had been treated with pre- and/or postemergence applications of allidochlor at locations in Quebec and Nova Scotia. The resulting residue data were made available to the regulatory agencies for registration purposes.

## MATERIALS AND METHODS

**Herbicide Treatments.** Leek samples for residue analysis were collected from two locations in Eastern Canada. At each location, both the treated and check plots were replicated 4 times.

Leeks, variety Giant Musselburg, were seeded on May 20, 1980, into 1.5 m × 7.7 m plots near the Agriculture Canada Research Station at Kentville, Nova Scotia. Prior to seeding, the plots were fertilized with 17–17–17 at 748 kg/ha. Three different allidochlor treatments were applied: a 6.75 kg/ha preemergence application on May 30; a 6.75 kg/ha preemergence application on May 30 followed by two 6.75 kg/ha postemergence applications, the first on July 18 when the crop was approximately 12 cm high (four to five leaf stage) and the second on Aug 14 when the crop was 25–30 cm high; a 13.0 kg/ha preemergence application of chlorthal (dimethyl tetrachloroterephthalate) on May 30 to control annual grasses and certain broad-leaved weeds followed by two 6.75 kg/ha postemergence applications of allidochlor, the first on July 18 and the second on Aug 14. The herbicide treatments were applied with a hand-held boom equipped with 8004 nozzles and operated at 186 kPa. Both chlorthal and allidochlor were applied in 500 L/ha water. On June 6, all of the plots were treated with the insecticide permethrin [3-phenoxybenzyl (±)-*cis,trans*-3-(dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] for cutworm control.

At the Station de Researche en Defence des Cultures, L'Assomption, Quebec, leeks, variety Helvetia, were seeded into 40-$m^2$ plots that had been previously fertilized with 10–10–10 at 400 kg/ha. Allidochlor was applied at 7.0 kg/ha preemergence on May 13 followed by a 7.0 kg/ha postemergence application of allidochlor on June 20 when the crop was at the three to four leaf stage. Both treatments were applied in 600 L/ha water using a small plot bicycle-type sprayer equipped with 8003 nozzles and operated at 200 kPa.

**Sampling.** The plots were randomly sampled at both locations until the sample size (0.25 kg at Kentville; 0.75 kg at L'Assomption) was obtained. The replicate samples were not pooled. Prior to being frozen, the leeks were prepared as if for table use or cooking. Roots were removed and the leaves trimmed prior to washing and then the samples were immediately frozen in polyethylene freezer bags. The samples were packed in dry ice when shipped to Regina and upon arrival stored in a freezer at -10 °C until extraction. Samples were collected on Sept 23 at L'Assomption and on Aug 29 and Oct 10 at Kentville.

**Chemicals.** All solvents were distilled-in-glass pesticide grade (Caledon Laboratories, Ltd., Georgetown, Ontario, Canada).

Florisil (Fisher Scientific), 60–80 mesh, was heated at 600 °C for 24 h and then deactivated by the addition of 5% water.

Sodium sulfate was heated at 600 °C for 48 h.

**Sample Extraction.** Twenty-five g of chopped leeks were blended in 100 mL of acetonitrile for 5 min at high speed in a 250-mL stainless steel blender jar. The blendate was filtered under reduced pressure through a coarse fritted glass Büchner funnel, followed by a 20 mL of acetonitrile rinse of the blender jar and a further 30-mL wash of the filter cake. The filtrate was then taken to volume (200 mL) with acetonitrile. The acetonitrile extract (40 mL; equivalent to 5 g of tissue) was transferred to a 500-mL separatory funnel containing 250 mL of 5% $Na_2SO_4$ solution. The mixture was extracted first with 100 mL and then 50 mL of methylene chloride, with each methylene chloride extract being passed through 30 mL of anhydrous sodium sulfate (contained on top of a glass wool plug in a 9-cm long-stemmed funnel) into a 250-mL round-bottomed flask. The sodium sulfate was finally washed with 25 mL of methylene chloride. The combined methylene chloride extracts were concentrated to approximately 5 mL by using a rotary evaporator, transferred to a 25-mL round-bottomed flask containing 15 mL of benzene, and then concentrated to approximately 1 mL by using a rotary evaporator to azeotropically remove any acetonitrile in the extract. Hexane (10 mL) was added to the flask and the solution concentrated to approximately 1 mL by using the rotary evaporator.

**Florisil Column Cleanup.** Deactivated Florisil (4.0 mL) was added to 10 mL of hexane in a 10 mm i.d. × 200 mm column and topped with 1 cm of anhydrous sodium sulfate, and the hexane was drained to the top of the sodium sulfate. The concentrated leek extract was transferred to the Florisil cleanup column followed by a 1.5-mL hexane rinse of the 25-mL round-bottomed flask. The column was then eluted with 45 mL of 2% acetone in hexane, the last 31 mL of which were concentrated to approximatly 0.5 mL with the rotary evaporator and then taken to volume (1 mL) with hexane for gas chromatographic analysis.

**Fortification.** Recoveries of allidochlor were determined by the extraction of leek tissue fortified at 100 ppb. Allidochlor (2.5 μg in 1 mL of methanol) was added to 25 g of chopped check leek tissue in a 50-mL beaker and the beaker placed in a fume hood. After the methanol had evaporated, the beaker was sealed with parafilm and placed in a refrigerator in the dark at 6 °C for 48 h prior to extraction. Six replicates were analyzed and the recoveries of allidochlor were determined from a standard calibration curve constructed by plotting nanograms of allidochlor against peak height.

**Gas Chromatography.** A Hewlett-Packard Model 5733A gas chromatograph, equipped with the Model 18789A nitrogen–phosphorus detector, was used with a Honeywell Electronik 194 recorder. The 1.2 m × 4 mm i.d. coiled glass column was packed with 5% Dexsil 300 on 80–100-mesh Chromosorb W, HP. The retention time for allidochlor was 3.7 min under the following operating conditions: helium (carrier gas), 35 mL/min; injector and column, 165 °C; detector, 300 °C. The detector voltage was set at approximately 16 V to give an offset of a 30% recorder deflection at attenuation ×32. Detector gas flow rates were, for hydrogen, 3.0 mL/min and, for air, 50 mL/min. A linear response was observed over the range 0.04–4.0 ng of allidochlor.

## RESULTS AND DISCUSSION

Modifications were made to the previously published method to avoid time-consuming evaporation stages and the use of benzene as an extractant. Samples were also analyzed by using a nitrogen-specific flame ionization

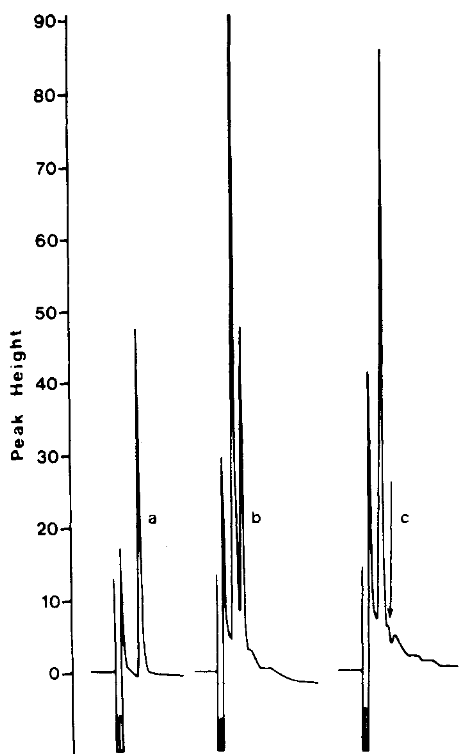


**Figure 1.** Chromatogram a, 2.0 ng of allidochlor (equivalent to 100 ppb) in hexane at attenuation ×8; chromatogram b, recovery from a leek check fortified at 100 ppb; chromatogram c, leek check.

detector (N-FID) rather than by microcoulometric detection using a chloride titration cell. Even though the allidochlor molecule contains only one nitrogen atom, the N-FID provided adequate sensitivity, with 4.2 ng of allidochlor giving a full-scale recorder deflection at attenuation ×8, range 1.

Analysis of the check samples showed only a small interfering peak at the retention time (3.7 min) for allidochlor (Figure 1, chromatogram c). The maximum interference from this peak, which appeared on the tail of a much larger background peak of retention time of 2.5 min, was 3–4 ppb, readily permitting a limit of detection of 100 ppb. The recovery of allidochlor from fortified leek check tissue, determined from six replicates that were analyzed at the 100-ppb fortification level, was 75.5 ± 6.3% (Figure 1, chromatogram b).

No significant differences in allidochlor residues were observed between preemergence and pre- plus postemergence applications or following a second postemergence application as residues in all samples regardless of treatment were less than 100 ppb. The registration of both pre- and postemergence applications of allidochlor for weed control in onions in Canada was based on allidochlor residues in the mature onions being less than 100 ppb (Bennet, 1983). In the present study, leeks that had been treated with similar applications of allidochlor at similar rates also had residues less than 100 ppb.

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**Registry No.** Allidochlor, 93-71-0.

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# Analysis of Coumestrol, a Phytoestrogen, in Alfalfa Tablets Sold for Human Consumption

Three locally available brands of commercial alfalfa tablets were analyzed for their coumestrol content by high-performance liquid chromatography and were found to contain from 20 to 190 ppm of this phytoestrogen. The recommended dosage of the alfalfa tablets that contain 190 ppm of coumestrol would provide greater than 1.1 mg/day coumestrol. These findings raise the possibility that those who take some brands of alfalfa tablets as a dietary supplement may be unwittingly receiving an unwelcome amount of this estrogenic hormone.

The presence in forage crops of naturally occurring nonsteroidal substances with estrogenic activity has been recognized for some time (Bradbury and White, 1954). Coumestrol, a benzofurocoumarin, is the predominant plant estrogen in alfalfa (Bickoff et al., 1964). A study of the relative potencies of five estrogen-like compounds commonly found in forages—coumestrol and the four isoflavones genistein, biochanin A, formononetin, and daidzein—showed coumestrol to be 35 times more potent than the most potent of the isoflavones as measured by the mouse uterine weight bioassay (Bickoff et al., 1962). By this same assay, coumestrol was some 200 times less potent than the animal estrogen, estrone, and almost 3000 times less potent than the synthetic estrogen, diethylstilbestrol. In spite of this apparent low level of potency, high levels of phytoestrogens in forage crops fed to cattle, sheep, and other animals have been found to result in deleterious biological effects, including increased teat

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