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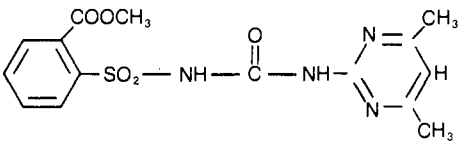
Analysis of the Herbicide Sulfometuron Methyl in Soil and Water by Liquid Chromatography

Edward W. Zahnow

An analytical method based on the use of a liquid chromatograph and a photoconductivity detector is described for sulfometuron methyl, methyl 2-[[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]benzoate, previously known as DPX-T5648, which is the active ingredient in Du Pont "Oust" herbicide. As little as 100 pg can be detected and measured after passage through the chromatographic column. Coupled with suitable extraction, cleanup, and isolation procedures, the method provides a means of determining sulfometuron methyl in soil and water at levels as low as 200 pg/g (0.2 ppb).

Du Pont "Oust" herbicide is effective in controlling many annual and perennial grasses and broad-leafed weeds on noncropland areas such as airports, fence rows, highways, lumber yards, petroleum tank farms, pipeline and utility rights-of-way, pumping installations, railroads, storage areas, and plant sites.

The active ingredient, sulfometuron methyl, methyl 2-[[[[(4,6-dimethyl-2-pyrimidinyl)amino]carbonyl]-amino]sulfonyl]benzoate is a sulfonylurea.



Sulfometuron Methyl

"Oust" may be applied under either pre- or postemergence conditions by using a wide variety of application rates (70–840 g/ha). The decomposition rate of the active ingredient, sulfometuron methyl, is very rapid under field conditions. Consequently, the methods developed to measure sulfometuron methyl in soil and water have a very low detection limit (0.2 ppb) to insure that the quantities of sulfometuron methyl which might be present are not sufficiently large to be injurious to agricultural crops. Derivatization of sulfometuron methyl is not required, and the operating conditions are sufficiently mild that decomposition is avoided.

A literature search revealed a number of methods that can be used for the analysis of sulfonylureas. If gas chromatography is to be used for the analysis, the sulfonylureas must be derivatized to more volatile and stable compounds by reacting the polar NH groups with dimethyl sulfate, methyl iodide, or diazomethane. Derivatization with diazomethane has been reported by Braselton et al. (1975, 1976, 1977), Midha et al. (1976), Taylor (1972), and Taylor et al. (1977). Maeda et al. (1981) have demonstrated that sulfonylureas can be determined by methylation with diazomethane followed by acylation with heptafluorobutyric anhydride. The use of dimethyl sulfate is described by Kleber et al. (1977), Prescott and Redman (1972), Sabih and Sabih (1970), and Simmons et al. (1972). An extractive methylation involving methyl iodide in methylene chloride is given in the paper by Hartvig et al. (1980).

A radioimmunoassay technique has been reported by Kajinuma et al. (1982) for the analysis of a sulfonylurea in serum.

Huck (1978) has developed a method in which sulfonylureas are hydrolyzed, converted to the dansyl derivative, separated by thin-layer chromatography, and detected by fluorescence.

A comparative study of gas chromatography and liquid chromatography has been made by Kimura et al. (1980) who found comparable sensitivity and reproducibility.

Methods for sulfonylureas based on liquid chromatography have been reported by Beyer (1972), Harzer (1980), Molins et al. (1975), Raghow and Meyer (1981), Reinauer et al. (1980), Robertson et al. (1979), Sved et al. (1976), Tsugi and Binns (1982), Uihlein and Sistovaris (1982), Waahlin-Boll and Melander (1979), and Weber (1976). Both normal and reverse-phase systems have been used, and it is not necessary to form derivatives since sulfonylureas generally give adequate response with ultraviolet absorbance detectors. Besenfelder (1981) has reported an improvement in sensitivity based on precolumn derivati-

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zation and fluorometric detection. However, the sensitivity requirements for sulfometuron methyl in soil and water are much greater than normally encountered, and in addition, extraction procedures used for soil analysis liberate substantial quantities of UV-absorbing substances from soil that interfere with the sulfometuron methyl determination.

To obtain adequate sensitivity and also eliminate undesirable responses from coextracted materials, use is made of the photoconductivity detector that is described in detail by Popovich et al. (1979). An application of this detector is discussed by McKinley (1981), and a modification of the reactor coil in the detector has been made by Ciccioli et al. (1981).

A similar detector has been described by Locke et al. (1982) which is very sensitive to aromatic hydrocarbons.

Pesticide residue analyses which make use of the photoconductivity detector have been reported by Büttler and Hörmann (1981), Zahnow (1982), Slates (1983), and Walters (1983). The photoconductivity detector is selective for molecules containing sulfur, halogen, nitrogen, and phosphorus atoms. Its sensitivity for sulfometuron methyl is about 50 times greater than can be achieved with the Du Pont 850 absorbance detector at 254 nm and 0.002 AUFS.

EXPERIMENTAL SECTION

Preliminary Treatment—Soil. All soil samples were air-dried for 2 or 3 days at room temperature in flat, stainless steel trays capable of holding at least 1-cm thicknesses of soil. These trays were lined with aluminum foil which was discarded after the drying operation to facilitate cleaning and minimize cross-contamination. If the soils were very damp, they were mixed periodically with a spatula. After drying, the samples were ball-milled, without added water, for 15–30 min depending on consistency, to insure homogeneity. These were then stored in a freezer until needed.

Extraction Procedure—Soil. A 50-g sample was weighed into a 250-mL polypropylene centrifuge bottle, and a mixture of 50 mL of methanol and 50 mL of aqueous 0.1 M Na_2CO_3–0.1 M $NaHCO_3$ (pH 10) was added. The mixture was shaken vigorously at room temperature with a wrist-action shaker for 1 h. The resulting slurry was centrifuged at 1500 rpm for 15 min to make a clean separation, and the supernatant liquid was decanted into a 500-mL separatory funnel. The mud cake remaining in the bottle was extracted again in the same manner, and the liquid was combined with that from the first extraction.

Cleanup Procedure—Soil. The aqueous solution was washed three times with 50-mL portions of chloroform by shaking gently for 1 min. Since the pK_A of sulfometuron methyl is about 5.7, the compound remained in the aqueous solution in its anionic form. The chloroform layers were discarded. A rotating tumbler unit was useful for this step and was operated at low speed. Care had to be taken with this operation to avoid the formation of an emulsion which was difficult to break. When a persistent emulsion did form, it could usually be broken by centrifuging. When centrifuging was necessary, only glass centrifuge bottles were used. Note: Chloroform is known to be a weak animal carcinogen. Polyvinyl alcohol gloves should be worn when handling this liquid, and adequate ventilation should be provided.

The aqueous solution was drained from the separatory funnel into a 400-mL beaker, and the pH was adjusted to 3–4 by adding 5% sulfuric acid *dropwise* while measuring with a calibrated pH meter. In this pH range sulfometuron methyl exists in the nonionic form and can be extracted into various organic liquids. The pH adjustment had to be performed carefully since a certain amount of foaming occurred. Also, due to the chemical equilibria involved, the pH changed slowly. If the final pH is too low, there is a danger of chemical decomposition of sulfometuron methyl, whereas if it is too high, extraction may be incomplete.

The solution was then transferred back into a 500-mL separatory funnel with 5 mL of distilled water being used to rinse the beaker. It was extracted three times with 50-mL portions of toluene by shaking vigorously for 1 min. When a rotating tumbler was used, it was operated at high speed. The toluene layers were separated from the aqueous phase and were then combined in a 200-mL pear-shaped flask. Again, when centrifuging was required to break an emulsion, only glass centrifuge bottles were used. The combined extracts were examined carefully to insure that they were free of water droplets.

To the toluene extract was added 1 mL of glacial acetic acid, and the solution was taken to dryness with a rotary evaporator at about 45 °C by using a water aspirator as the vacuum source.

The residue was dissolved with five washings of about 1 mL each of solution C (750 parts by volume of cyclohexane, 125 of 2-propanol, and 125 of methanol). These washings were collected in a 10-mL centrifuge tube. A gentle stream of nitrogen was used to evaporate this combined solution to dryness at room temperature. The sample was stored dry in a refrigerator until it was to be analyzed.

At that time the sample was dissolved in solution C with dilution to a final volume of 1 mL. The entire sample was filtered into a small vial by using a Millex-SR 0.5 μm filter unit (Millipore Corporation) mounted on a 1-mL hypodermic syringe. These filter units were discarded after each use.

Isolation and Cleanup Procedure—Water. A 50-g sample was weighed in a 100-mL beaker, after which the pH was adjusted to 3.5 by adding 0.1 N HCl dropwise, measuring the pH with a calibrated pH meter. Then 5 mL of methanol was added, and the resulting solution was mixed thoroughly.

This solution was put through a C2 Bond Elut column (500 mg/2.8 mL, Analytichem International) which had been previously washed with 10 mL of methanol followed by 25 mL of a mixture of nine parts of water (pH 3.5) and one part of methanol. Next the column was washed with 10 mL of the mixture of nine parts of water (pH 3.5) and one part of methanol. Up to this point all effluents were discarded. Following this step, the column was eluted with 8 mL of ethyl acetate, and this liquid was collected in a 15-mL centrifuge tube. (Note: Liquids were pulled through the Bond Elut column by applying vacuum. The flow rate was such that discrete drops could be seen coming from the column.) In the cases where a water layer was found in the centrifuge tube, the ethyl acetate layer (upper) was removed with a Pasteur capillary pipette and placed into a 10-mL centrifuge tube. A gentle nitrogen stream was used to evaporate the ethyl acetate solution to dryness at 40 °C. The sample was stored dry in a refrigerator until it was to be analyzed.

For analysis, the sample was dissolved in solution C with dilution to a final volume of 1 mL. The entire sample was then filtered into a small vial with a 0.5-μm filter unit mounted on a 1-mL hypodermic syringe. These filter units should be discarded after each use.

Liquid Chromatography. Since the photoconductivity detector (Tracor Model 965) must be used at its maximum

sensitivity to achieve the desired lower detection level, it was essential that the chromatographic system provided good temperature control of the column and reasonably pulse-free delivery of mobile phase to minimize base line fluctuations.

The photoconductivity detector must be used for this analysis to obtain adequate sensitivity and selectivity. The mercury lamp was used in the detector since it provided much greater sensitivity than the zinc lamp. The detector, including the lamp, was left on at all times to insure greater stability. The flow of the mobile phase through the reference and analytical loops was balanced to within ±5%. This was accomplished by installing a metering valve in the solvent line which exits from the reference compartment of the conductivity cell. The "T" that brought the two solvent lines from the conductivity cell back together was eliminated from the instrument. Also, the ion exchange resin tube was not needed to purify the mobile phase and might actually have introduced unwanted materials into the system had it not been removed.

The mobile phase consisted of a mixture of 920 mL of solution C and 80 mL of solution B (1000 parts by volume of 2-propanol, 1 of glacial acetic acid, and 1 of water). Solution B and mobile phase were prepared only as needed.

The column was a Du Pont Zorbax SIL (25 cm × 4.6 mm) controlled at 35 °C. A new column had to be conditioned by pumping solution A (10 parts by volume of 2-propanol, 10 of methanol, 5 of glacial acetic acid, and 1 of water) through it for several hours at 1 mL/min. This treatment was also used to clean columns which had started to lose their efficiency because of contamination from samples. A contaminated column was characterized by broad peaks which tailed very badly and by shifting retention times. This conditioning solvent must be thoroughly flushed from the column with the mobile phase. An hour of flushing at 0.5 mL/min was usually sufficient.

A sample valve was a used for manual injection of standards and samples, and the loop volume was 10 μL to minimize contamination of the HPLC column and broadening of the chromatographic peaks.

During normal operation mobile phase was pumped through the column at 0.5 mL/min, which was judged to be the minimum practical rate. At this flow rate sulfometuron methyl eluted from the column in 16–17 min, depending on the extent of the column deactivation. This rate was selected because the detector response increased with decreasing flow rate due to the longer residence time of the sample in the quartz reactor coil.

Standardization. A standard stock solution of sulfometuron methyl was prepared by weighing out 10.0 mg, dissolving it in methylene chloride, and diluting to 100 mL in a volumetric flask. This solution was quite stable and can be stored for many months. It should be stored in a refrigerator. Long-term storage and repeated use of this solution may result in the evaporation of some methylene chloride, thereby increasing the concentration of sulfometuron methyl.

The working standards used for liquid chromatography as well as for the spiking of recovery samples were prepared by pipetting 1.0 mL of the stock solution into a clean, dry, 100-mL volumetric flask, evaporating the methylene chloride with a gentle nitrogen stream, dissolving the residue in solution C, and diluting to volume with solution C. Standards with concentrations of 0.50, 0.20, 0.10, 0.05, 0.02, and 0.01 μg/mL were prepared from the 1.0 μg/mL standard by appropriate dilution with solution C. The set of standards prepared in solution C was replaced with a fresh set every month. Over this time period no change in detector response was observed. All standards were stored in a refrigerator when not in use.

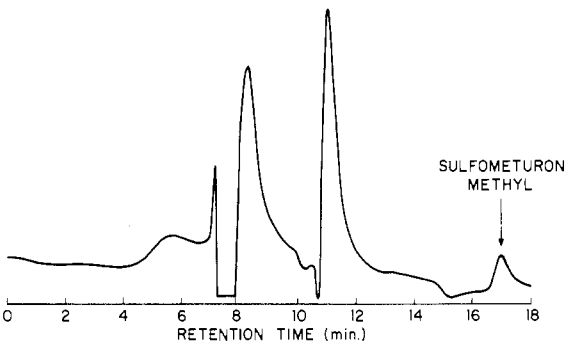

Figure 1. Chromatogram of sulfometuron methyl at a detection limit of 100 pg (detector sensitivity 1 × 1).

RESULTS AND DISCUSSION

The detector output was linear over this particular weight range of sulfometuron methyl, and the average response factor was 184 mm/ng with a standard deviation of 5 mm/ng. The minimum detectable quantity of sulfometuron methyl put through the chromatography column was 100 pg, and this amount produced a peak 19 mm in height when the detector was operated at maximum sensitivity (1 × 1) by using a 1-mV recorder with a chart width of 25 cm as the readout device.

Figure 1 is a chromatogram of sulfometuron methyl obtained by injecting 10 μL of the 0.01 μg/mL standard. The detector sensitivity was at its maximum value (1 × 1), and the chromatographic peak shown represents the detection limit of the method as displayed on a 25-cm chart. Normally, the short-term noise is <1 mm (peak to peak). To achieve this sensitivity it is necessary to use a column of high efficiency and also a pump that produces only small pressure pulses. Also, the detector lamp usually needs to be replaced after 500–1000 h of operation, and periodic ultrasonic cleaning of the conductivity cell and electrodes with 10% phosphoric acid is required.

For the recovery study of soil, Athena silt loam from St. John, WA (pH 7.1; USDA sand, 13%; USDA silt, 69%; USDA clay, 18%; organic content, 3.5%) and Woodstown sandy loam from Dover, DE (pH 4.9; USDA sand, 65%; USDA silt, 29%; USDA clay, 6%; organic content, 1.3%) were used primarily. These soils were fortified at three levels, from the detection limit to a value 100 times greater. Eight replicates were made at each fortification level for each soil. At 0.2 ppb fortification the recovery from Athena silt loam was 76% (S. D. 11%) and from Woodstown sandy loam it was 80% (S. D. 13%). At 2.0 ppb fortification the respective recoveries were 93% (SD 19%) and 81% (SD 9%), whereas at 20 ppb fortification they were 87% (SD 4%) and 79% (SD 7%), respectively.

The chromatograms of an extract of untreated Athena silt loam and of an extract of this soil fortified at 0.2 ppb of sulfometuron methyl are shown in Figure 2. The lower trace (A) is that of the control extract, and the upper trace (B) is that of the 0.2 ppb fortified sample. The measured recovery was 75%.

To establish the reliability of this method for the analysis of sulfometuron methyl in soil, a set of field samples, treated one year before sampling, was analyzed. These results are compared in Table I with results obtained on the same samples by a corn-root bioassay test by Hutchison (1982) which will detect very low levels of sulfometuron methyl in soil. The two sets of results show a good correlation. Recovery measurements made on

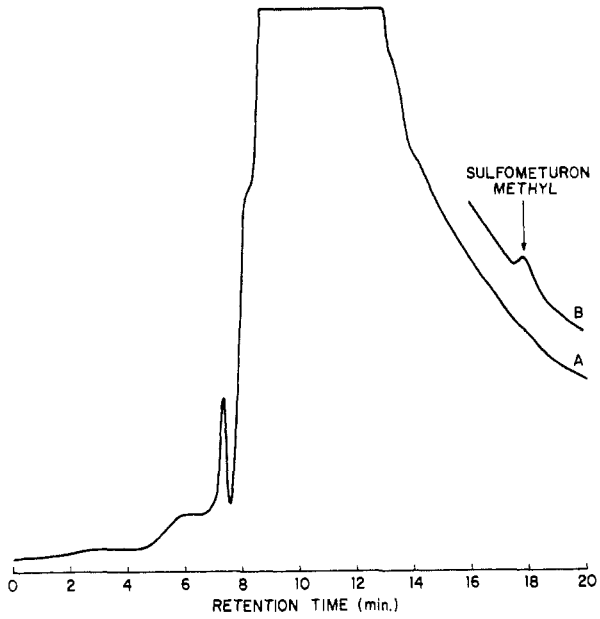

Figure 2. Chromatograms of Athena silt loam extracts: (A) control; (B) 0.2 ppb fortification (detector sensitivity 1 × 1).

Table I. Comparative Measurements of Sulfometuron Methyl in Soil[a]

treatment, kg/ha	depth, cm	sulfometuron methyl, ppb: HPLC assay	sulfometuron methyl, ppb: corn-root bioassay
0.03	0–10	0.5	0.2–0.3
0.03	10–20	0.2	<0.05
0.03	20–30	<0.2	<0.05
0.125	0–10	1.0	>1.0
0.125	10–20	0.5	0.5–1.0
0.125	20–30	<0.2	NA[b]
0.500	0–10	2.1	>1.0
0.500	10–20	0.6	0.2–0.3
0.500	20–30	0.6	0.5–1.0

[a] Keyport silt loam, Newark, DE; pH 5.60; sand (USDA), 4%; silt (USDA), 86%; clay (USDA), 10%; organic content, 2.7%. [b] Not available because of sample loss.

samples fortified from 0.2–2.0 ppb averaged 86%.

For the recovery study of water, laboratory distilled and a sample from Stoney Run (New Castle County, DE) were fortified and analyzed. The fortification range was from the detection limit to a value 100 times greater. Ten replicates were made at each fortification level for each type of water except for the case of the 0.2 ppb fortification of laboratory distilled, which had 8 replicates. At 0.2 ppb fortification the recovery from laboratory distilled was 103% (SD 4%) and from Stoney Run it was 99% (SD 10%). At 2.0 ppb fortification the respective recoveries were 102% (SD 8%) and 96% (SD 4%), whereas at 20 ppb fortification they were 98% (SD 7%) and 96% (SD 4%), respectively. These results demonstrate essentially quantitative recovery at all levels.

The chromatograms of an extract of untreated Stoney Run water and of an extract of this water fortified at 0.2 ppb of sulfometuron methyl are shown in Figure 3. The lower trace (A) is that of the control extract, and the upper trace (B) is that of the 0.2 ppb fortified sample. In this case the calculated recovery was 107%.

CONCLUSION

Sulfometuron methyl, which is the active ingredient in "Oust" herbicide, can be effectively measured in soil and water. The limit of detection is 0.2 ppb when a normal-phase HPLC separation is used with the highly sensitive and selective photoconductivity detector. A bioassay method has been applied to the soil analysis to establish the accuracy of this method.

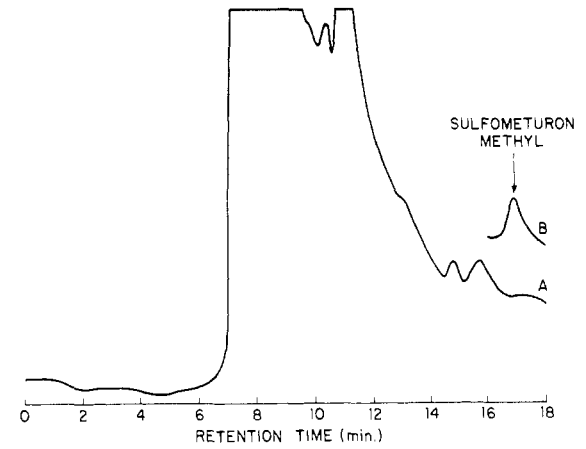

Figure 3. Chromatograms of Stoney Run water extracts: (A) control; (B) 0.2 ppb fortification (detector sensitivity 1 × 1).

Registry No. Sulfometuron methyl, 74222-97-2; water, 7732-18-5.

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Persistence and Transformation of the Herbicides [^{14}C]Fenoxaprop-ethyl and [^{14}C]Fenthiaprop-ethyl in Two Prairie Soils under Laboratory and Field Conditions

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The experimental herbicidal esters fenoxaprop-ethyl (ethyl 2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propanoate) and fenthiaprop-ethyl (ethyl 2-[4-[(6-chloro-2-benzothiazolyl)oxy]phenoxy]propanoate) both underwent almost complete hydrolysis, within 24 h, to their respective acids in soils with moisture contents greater than 65% of field capacity. In air-dried soils, ester hydrolysis was considerably less. The fate of the two ^{14}C-labeled esters was studied in two soil types under laboratory and field conditions. Each herbicide gave rise to the same transformation products in the laboratory and field studies. [^{14}C]Fenthiaprop acid and its corresponding transformation products (a phenetole, a phenol, and a benzazolone) have a soil persistence of about twice that of [^{14}C]fenoxaprop acid and corresponding transformation products.

The structurally related herbicides HOE 33171, whose proposed common name is fenoxaprop-ethyl (**1**) and HOE 35609, with the proposed common name of fenthiaprop-ethyl (**6**), are currently being evaluated on the Canadian prairies, at rates less than 0.5 kg/ha, as postemergence herbicides for the control of grassy weeds in a variety of broad-leafed crops.

Although these chemicals are applied to the growing crops, some of the herbicidal sprays inevitably come into contact with the soil making it necessary to determine their fate in soil. Currently nothing has been reported regarding fenoxaprop-ethyl and fenthiaprop-ethyl in soils; thus, the studies to be described were undertaken to investigate the rate of hydrolysis of the herbicidal esters to their respective acids in two Saskatchewan soils and to investigate the persistence and transformation of [^{14}C]fenoxaprop-ethyl and [^{14}C]fenthiaprop-ethyl in the two soil types under both laboratory and field conditions.

MATERIALS AND METHODS

Soils. Field plots were situated on a sandy loam of the Asquith Association, classified as a Dark Brown Chernozemic, Orthic Dark Brown, and on a heavy clay of the Regina Association, classified as a Dark Brown Chernozemic, Rego Dark Brown. The composition and physical characteristics of these soils have already been described (Smith and Muir, 1980).

For the laboratory studies, soil samples were collected from the 0–5-cm soil horizons at both locations during the fall of 1982. After screening through a 2-mm sieve, the soils were immediately used for the laboratory experiments.

Chemicals. Fenoxaprop-ethyl (**1**) uniformly labeled with ^{14}C in the chlorophenyl ring, with a specific activity of 28.3 mCi/g and a radiochemical purity of over 99%, was provided by Hoechst Aktiengesellschaft, Frankfurt, Germany, as was the similarly labeled fenthiaprop-ethyl (**6**) which had a specific activity of 22.56 mCi/g and a radiochemical purity in excess of 99%. The radioactive chemicals were dissolved in methanol (10 mL) to prepare solutions containing 8.00 μCi/mL (300 μg/mL) of the oxygenated herbicide and 9.10 μCi/mL (400 μg/mL) of the thio herbicide.

In addition to nonlabeled samples of the two herbicidal esters, samples of the following nonradioactive standards were provided by Hoechst: 2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propionic acid (**2**); 2-[4-[(6-chloro-2-benzothiazolyl)oxy]phenoxy]propionic acid (**7**); 4-[(6-chloro-2-benzoxazolyl)oxy]phenetole (**3**); 4-[(6-chloro-2-benzothiazolyl)oxy]phenetole (**8**); 4-[(6-chloro-2-benzoxazolyl)oxy]phenol (**4**); 4-[(6-chloro-2-benzothiazolyl)-oxy]phenol (**9**); 6-chlorobenzoxazolone (**5**); and 6-chlorobenzothiazolone (**10**).

Short-Term Hydrolysis Study. Duplicate samples (20 g) of moist heavy clay and sandy loam at 20%, 65%, and 100% of their field capacity moisture levels were weighed into 125-mL glass-stoppered flasks and treated with 20 μL of a solution containing 1 mg of the respective ethyl ester per mL of methanol. Separate soil treatments were made for each herbicide. This application rate was equivalent to 1.0 ppm herbicide based on moist soil weight. The soils were stirred to distribute the chemicals, before the flasks were sealed and incubated in the dark at 20 ± 1 °C. All soil samples were extracted and analyzed gas chromatographically after 24 h to determine amounts of the ethyl esters remaining.

Ester Extraction and Analysis. To each flask was added sufficient 20% aqueous acetonitrile containing 2.5% of glacial acetic acid so that the total volume of extractant together with water present in the soils was equivalent to 50 mL. The flask and contents were shaken on a wrist-action shaker for 1 h. Following centrifugation at 3500 rpm for 4 min, 25 mL of the supernatant was added to 5% aqueous sodium carbonate (100 mL) and shaken in a 250-mL separatory funnel with *n*-hexane (25 mL). The organic phase was collected in a 50-mL glass-stoppered tube and dried over sodium chloride, and 5-μL portions examined gas chromatographically for esters remaining.

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