A Multiresidue Method for the Analysis and Verification of Several Herbicides in Water

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An analytical method to determine and verify residues of both neutral and acidic herbicides in water is presented. Acidic herbicides were derivatized by using diazomethane. Recoveries of seven commonly used herbicides from distilled water at fortification levels of 0.1–1 ppb ranged from 80 to 117%. Except for MCPA, all other herbicide residues could be verified by using two different detector modes. The method was used successfully in a preliminary study to monitor herbicide residues in irrigation return flow waters.

INTRODUCTION

Herbicides are used extensively to control grasses and broad-leaved weeds in crops and to control brush on rangeland and along rights-of-way. Because of such extensive and widespread use, it can be to expected that water bodies within the treated areas could become contaminated with the more commonly used herbicides. Contamination of lakes, rivers, streams, sloughs, and farm dugouts from agricultural uses of herbicides could occur from direct application, herbicide drift and subsequent deposition, snow melt and rainfall runoff, and the return of waste waters from irrigation sites to receiving waters.

Because of the diversity in herbicide products available to farmers for weed and brush control, environmental water samples would be best analyzed for herbicide residues by using a multiresidue procedure. Two multiresidue analytical methods for the determination of herbicide residues at the ppt and ppb levels in water have been published recently, one method for acidic herbicides (Agemian and Chau, 1977) and the other for herbicides with neutral properties (Lee and Chau, 1983). In the study concerning acidic herbicides, both pentafluorobenzyl and 2-chloroethyl esterification procedures were employed to enhance sensitivity to electron-capture detection. The second study concerning neutral herbicides unnecessarily included esters of acidic herbicides which, although neutral as parent compounds, have hydrolysis half-lives in the order of 24–48 h and thus in terms of residue analysis are invariably present in the environment as the corresponding acids (Bailey et al., 1970; Rodgers and Stalling, 1972; Smith, 1972, 1976; Smith and Hayden, 1980; Grover, 1973; Zepp et al., 1975). The purpose of the present study was to develop a multiresidue analytical procedure to determine residues of several commonly used herbicides, both neutral and acidic, in water samples. In addition the more commonly used diazomethane esterification was employed, and as well, the use of specific detectors for confirmation and to optimize sensitivity was evaluated.

Seven herbicides (Table I) were studied and a comparison was made of recoveries from fortified distilled water when analyzed by two analysts. The method was successfully used in a preliminary monitoring of residues of these herbicides in return flow water samples collected from two major drainage ditches in the Outlook Irrigation District at Outlook, SK, during the 1981 irrigation season.

MATERIALS AND METHODS

Chemicals. All solvents were pesticide grade (Caledon Laboratories Ltd., Georgetown, ON, Canada). Florisil (Fisher Scientific Co., Toronto, ON, Canada), 60–100 mesh, was heated at 600 °C for 24 h and then deactivated by the addition of distilled water (5%). Sodium sulfate was heated at 600 °C for 48 h.

Caution! Diazomethane is very toxic and should be prepared and used in a well ventilated fume hood. Contact of ground glass apparatus with diazomethane, which is also explosive, should be avoided. *N*-Methyl-*N'*-nitro-*N*-nitrosoguanidine (MNNG, Aldrich Chemical Co. Inc., Milwaukee, WI), a precursor of diazomethane, is a cancer suspect agent and a very potent mutagen.

Fortification. Two stock solutions of all seven herbicides dissolved in acetone were prepared and stored in amber volumetric flasks. In one solution, all herbicides were present at 1.0 μg/mL, except for MCPA at 10.0 μg/mL. In the second solution, the concentrations were as follows: dicamba, 2,4-D, bromoxynil, and picloram, 0.5 μg/mL; triallate and trifluralin, 0.1 μg/mL; MCPA, 1.0 μg/mL. The water samples were fortified by the addition of 1 mL of stock solution to 1 L of distilled water. Six replicates were prepared from each stock solution and were extracted immediately after preparation by two analysts, with each analyst extracting half of the fortified samples at each of the two fortification levels.

Water Sample Extraction. (a) Analysis for triallate and trifluralin. Fortified water (1 L) was transferred to a 2-L separatory funnel and 2.0 mL of 20% NaOH solution was added to give a pH of approximately 12. The water was extracted by shaking twice for 1 min with 100 mL of hexane (emulsions can be broken by adding a few drops of isopropyl alcohol), with each hexane extract being passed through 30 mL of anhydrous sodium sulfate (contained in a 9-cm diameter long-stemmed funnel on top of a glass wool plug) into a 500-mL round-bottom flask, followed by a 25-mL hexane wash of the sodium sulfate. The combined hexane extracts were then concentrated to approximately 10 mL by using a rotary evaporator, transferred to a 25-mL round-bottom flask, and further concentrated to approximately 1 mL. The alkaline aqueous phase was kept in the 2-L separatory funnel for further analysis.

Florisil (4.0 mL) was added to 10 mL of hexane in a 7 mm id × 200 mm column and topped with a 1-cm layer of anhydrous sodium sulfate, and the hexane drained to the top of the sodium sulfate layer. The concentrated extract residue was transferred to the cleanup column followed by two 1.5-mL hexane rinses of the 25-mL round-bottom flask. The column was then eluted (1 mL/min) with 25 mL of 0.5% acetone in hexane, the first 9 mL of which was discarded and the remainder collected in a 50-mL graduated centrifuge tube and then concentrated to approximately 6 mL with a nitrogen evaporator.

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Table I. Common, Commercial, and Chemical Names of the Seven Herbicides

common name	commercial name	chemical name
bromoxynil	Buctril, Torch, Brominal	3,5-dibromo-4-hydroxybenzonitrile
2,4-D	Weedar, Weedone, Esteron	(2,4-dichlorophenoxy)acetic acid
dicamba	Banvel	3,6-dichloro-*o*-anisic acid
MCPA	MCP	[(4-chloro-*o*-tolyl)oxy]acetic acid
picloram	Tordon	4-amino-3,5,6-trichloropicolinic acid
triallate	Avadex BW	*S*-2,3,3-trichloroallyl diisopropylthiocarbamate
trifluralin	Treflan	α,α,α-trifluoro-2,6-dinitro-*N*,*N*-dipropyl-*p*-toluidine

The concentrated extract was finally taken to volume (10 mL) with hexane for gas chromatographic analysis of triallate and trifluralin.

(b) Analysis for MCPA, 2,4-D, bromoxynil, dicamba, and picloram. Sodium chloride (200 g) was added to the alkaline aqueous phase in the 2-L separatory funnel and the mixture was shaken unitl all of the NaCl dissolved. Concentrated sulfuric acid (2.0 mL) was added to give a pH <2 and the acidified aqueous phase was extracted twice with 100 mL of diethyl ether. Each ether extract was passed through 30 mL of anhydrous sodium sulfate (contained in a 9-cm diameter long-stemmed funnel on top of a glass wool plug) into a 500-mL round-bottom flask, followed by a 50-mL ether wash of the sodium sulfate. The combined ether extracts were concentrated to approximately 3 mL with a rotary evaporator and transferred to a 50-mL graduated centrifuge tube along with three 3-mL ether rinses of the 500-mL round-bottom flask. (Caution: the ether extract should be checked for the presence of peroxides prior to concentration.) The combined ether extract was then concentrated to 1–2 mL with a gentle stream of nitrogen.

Diazomethane in ether was prepared by using a generator (catalogue no. Z10, 159-1, Aldrich Chemical Co. Inc., Milwaukee, WI), according to the manufacturer's directions. Diazomethane solution (2 mL) was added to the concentrated ether extract and the reaction mixture was left at room temperature for 15 min. Hexane (1.5 mL) was then added and the mixture was concentrated to approximately 1 mL with a stream of nitrogen. The addition of hexane and subsequent concentration was repeated two more times.

The concentrated extract was transferred to a Florisil cleanup column (prepared as described for the analysis of triallate and trifluralin) along with a 1.5-mL hexane rinse of the 50-mL centrifuge tube. The column was then eluted with 40 mL of 0.5% acetone in hexane, the first 10 mL being discarded and the remainder collected and then concentrated to approximately 6 mL with either a rotary evaporator or a stream of nitrogen. The concentrated eluate was then taken to volume (10 mL) with hexane for gas chromatographic analysis of the methyl esters of 2,4-D, MCPA, and dicamba as well as the methyl ether of bromoxynil. The Florisil column was then eluted with 45 mL of 5% acetone in hexane, the first 10 mL being discarded and the remainder collected, concentrated, taken to volume as described above, and then gas chromatographically analyzed for picloram methyl ester.

Gas Chromatography. (a) Electron-capture detection. A Tractor Model 560 gas chromatograph equipped with a ^{63}Ni linearized electron-capture detector was used with a Hewlett Packard Model 3380A integrator. The 1.8 m × 4 mm id coiled glass column, packed with 100–200 mesh Ultrabond (RFR Corp., Hope, RI), was used under the following operating conditions: 95% argon–methane (carrier gas), 30 mL/min; detector, 300 °C; injector, 220 °C. The retention times and the corresponding column temperatures used were as follows: trifluralin (3.6 min), triallate (5.2 min), column 180 °C; methyl derivatives of dicamba (3.4 min), MCPA (4.7 min), bromoxynil (6.6 min), and 2,4-D (7.5 min), column 170 °C; picloram methyl ester (8.2 min), column 225 °C. A linear response over the range 0.04–4.0 ng was observed for all compounds, except MCPA methyl ester.

(b) Electrolytic conductivity detection. A Tractor Model 560 gas chromatograph, equipped with a Hall Model 700A electrolytic conductivity detector operated in the halogen mode, was used with a Perkin-Elmer Model 56 1-mV recorder. A 1.8 m × 4 mm id coiled glass column, packed with 100–200 mesh Ultrabond, was used with the following operating conditions: helium (carrier gas), 35 mL/min; injector, 220 °C; furnace base, 250 °C; furnace, 910 °C; reaction gas (hydrogen), 70 mL/min; conductivity solvent (*n*-propyl alcohol), 0.6 mL/min; vent time, 0.75 min. The retention times and corresponding column temperatures were as follows: methyl derivatives of dicamba (2.3 min), MCPA (3.2 min), bromoxynil (4.0 min), and 2,4-D (4.8 min), column 190 °C; picloram methyl ester (8.2 min), column 225 °C. Linear responses were observed over the range 0.4–40.0 ng for MCPA methyl ester and 0.04–4.0 ng for the other derivatives.

(c) N-Specific, alkali-ionization detection. A Hewlett Packard Model 5733A gas chromatograph, equipped with a Model 18789A nitrogen–phosphorous FID detector, was used with a Honeywell Electronik 194 1-mV recorder. A 1.2 m × 4 mm id coiled glass column, packed with 10% OV-1 on 80–100 mesh Chromosorb G, HP, was used under the following conditions: helium (carrier gas), 35 mL/min; injector and column, 225 °C; detector, 300 °C; detector gases, hydrogen, 3.0 mL/min, and air, 50 mL/min. The detector voltage was set at approximately 15 V and gave an offset of a 25% recorder deflection. The retention times for trifluralin and triallate were 2.8 and 4.3 min, respectively, and linear responses for both compounds were observed over the range 0.04–4.0 ng.

Water Sample Collection. Water samples were collected at weekly intervals from three locations in the Outlook Irrigation District at Outlook, SK. The pumping station (M1) on Lake Diefenbaker, the source of the irrigation water, was one collection site (May 28–June 16) and the others (May 28–July 15) included two major drainage ditches (1C and 6C) which returned the return flow waters from flood or gravity irrigated fields to the South Saskatchewan River. Duplicate water samples, collected in 1-L brown glass bottles, were extracted within 24 h of collection. Prior to extraction, the entire water sample (approximately 1040 mL) was filtered under reduced pressure through a Buchner funnel (7 cm) equipped with a glass fiber filter paper.

RESULTS AND DISCUSSION

The analytical method as outlined in Figure 1 permitted the analysis of both neutral and acidic herbicides and should also be suitable for the analysis of several other currently used herbicides of either type. For example, subsequent work has shown that residues of diclofop [2-[4-(2,4-dichlorophenoxy)phenoxy]propionic acid] can be determined by using this method, and that extraction

Table II. Recoveries of Seven Herbicides from Fortified 1-L Water Samples by Two Analysts

herbicide	amt added, μg/L	percent recovery[a] analyst 1	analyst 2
bromoxynil	1.0	99.7 ± 0.6	96.3 ± 2.5
	0.5	112.8 ± 6.5	104.0 ± 7.2
2,4-D	1.0	89.3 ± 11.6	101.3 ± 18.6
	0.5	116.7 ± 22.7	105.3 ± 12.8
dicamba	1.0	97.8 ± 5.3	97.0 ± 4.4
	0.5	112.8 ± 6.5	95.0 ± 7.5
MCPA	10.0	101.0 ± 9.5	98.0 ± 2.6
	1.0	96.3 ± 4.6	100.0 ± 0.0
picloram	1.0	97.0 ± 2.6	102.7 ± 5.5
	0.5	82.0 ± 3.5	82.7 ± 7.6
triallate	1.0	96.0 ± 4.0	111.0 ± 15.6
	0.1	103.3 ± 11.5	100.0 ± 10.0
trifluralin	1.0	80.3 ± 1.2	81.7 ± 11.6
	0.1	80.0 ± 0.0	93.3 ± 5.8

[a] t = 0.637. Percent recovery values for each analyst are the mean of three determinations.

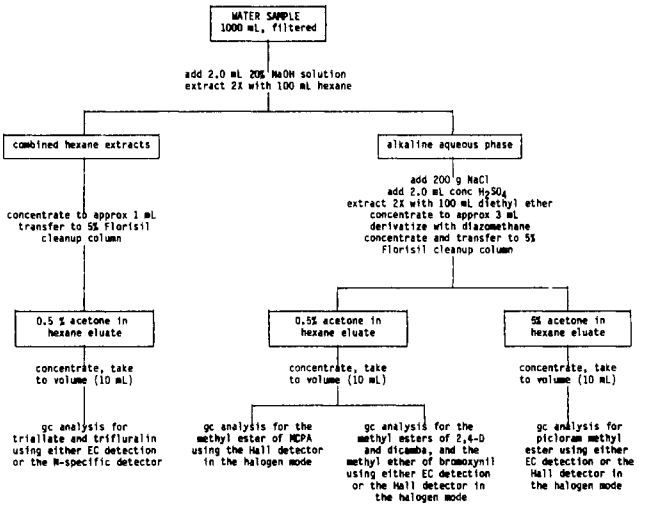

Figure 1. Flow sheet of the analytical method.

of neutral herbicides with methylene chloride (Lee and Chau, 1983) permits analysis of triazine herbicides such as atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine] as well.

Recoveries from fortification experiments were determined by electron-capture detection for all herbicides except MCPA. Because of poor sensitivity to electron-capture detection (Figure 2, chromatogram c), MCPA methyl ester was detected by using the Hall electrolytic conductivity detector in the halogen mode. Recoveries of all seven herbicides were good at both fortification levels and ranged from 80 to 117% (Table II). Recovery reproducibility by two analysts proved to be excellent, the differences being insignificant when using the paired t test. Gas chromatographic analysis of distilled water blanks did not show any significant interferences for any of the herbicides studied and the limits of detection ranged from 0.1 to 1.0 ppb (Table II).

In the absence of the availability of mass spectrometric detection for confirmation purposes, the presence of both trifluralin and triallate can be readily confirmed by using N-specific alkali-ionization detection. Similarily, residues of dicamba, 2,4-D, bromoxynil, and picloram can also be verified as their respective methyl derivatives with the Hall electrolytic conductivity detector in the halogen mode. Confirmation with the specific detectors could be carried out at the same limits of detection as those attained by using electron-capture detection. The only herbicide for which confirmation is not possible by an alternate detection method was MCPA.

The method was then used in a preliminary study in which herbicide residues in irrigation return flow waters at the Outlook Irrigation District were monitored. Since only a minimal amount of MCPA and no picloram were used within the Irrigation District, analysis for these herbicides was not carried out. The supply water from the pumping station, monitored to provide background interferences for the various herbicides, consistently showed trace interferences at the retention time for 2,4-D which were less than the limit of detection (Table III). For the first two weeks of sampling, these interferences in the return flow water samples from the 1C and 6C drainage ditches reflected what was found in the supply water. The average background interference in the 2,4-D region of the chromatogram was 0.13 ppb whereas those for the dicamba and bromoxynil regions were less than 0.1 ppb in both the supply water and in drainage ditch water prior to the commencement of spraying which occurred after the June 4 sampling. These backgrounds still permitted a limit of detection of 0.5 ppb for all three herbicides. The background interferences in the trifluralin and triallate regions were consistently less than 0.01 ppb and readily permitted

Table III. Herbicide Residues (ppb) Found in Duplicate Samples of the Return Flow Waters of the 1C and 6C Drainage Ditches in the Outlook Irrigation District[a]

date	location	2,4-D		dicamba		bromoxynil	
May 28	M1	0.17	<0.10	<0.10	<0.10	<0.10	<0.10
	1C	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
	6C	0.11	0.13	<0.10	<0.10	<0.10	<0.10
June 4	M1	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
	1C	<0.10	0.11	<0.10	<0.10	<0.10	<0.10
	6C	0.15	<0.10	<0.10	<0.10	<0.10	<0.10
June 11	M1	0.12	0.22	<0.10	<0.10	<0.10	<0.10
	1C	0.30	0.42	<0.10	<0.10	1.76	1.98
	6C	0.27	0.29	<0.10	<0.10	<0.10	<0.10
June 16	M1	0.12	0.13	<0.10	<0.10	<0.10	<0.10
	1C	1.54	1.48	<0.10	<0.10	0.91	0.89
	6C	0.19	0.26	<0.10	<0.10	0.42	0.41
June 25	1C	9.39	9.39	<0.10	<0.10	<0.10	<0.10
	6C	0.10	0.15	<0.10	<0.10	<0.10	<0.10
July 2	1C	2.92	3.01	<0.10	<0.10	0.34	0.32
	6C	0.44	0.59	<0.10	<0.10	<0.10	<0.10
July 9	1C	0.95	0.92	0.34	0.27	0.56	0.56
	6C	0.27	0.22	<0.10	<0.10	0.18	0.11
July 15	1C	1.01	1.03	0.19	0.16	0.14	0.13
	6C	0.67	0.65	<0.10	<0.10	<0.10	<0.10

[a] Residues less than 0.5 ppb (limits of detection) have been included to indicate background interferences.

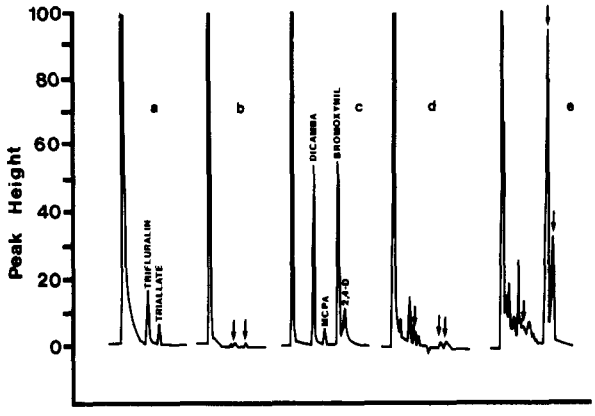

Figure 2. All chromatograms are from electron-capture detection and were recorded at attenuation ×2. Chromatogram a: analytical standard equivalent to 0.1 ppb trifluralin and triallate; chromatogram b: June 4 supply water sample showing background interferences of the region of trifluralin and triallate; chromatogram c: analytical standard equivalent to 0.5 ppb dicamba, bromoxynil, and 2,4-D methyl derivatives and 50 ppb MCPA methyl ester; chromatogram d: May 28 C6 drainage water sample showing background interferences in the regions of the methyl derivatives of dicamba, bromoxynil, and 2,4-D, respectively; chromatogram e: June 16 C1 drainage ditch water sample showing a trace, 0.91 and 1.54 ppb, of methyl derivatives of dicamba, bromoxynil, and 2,4-D, respectively.

the limit of detection of 0.1 ppb. Typical background interferences in the regions of trifluralin and triallate and the methyl derivatives of 2,4-D, dicamba, and bromoxynil are shown in Figure 2. After spraying was begun, residues of 2,4-D and bromoxynil greater than 0.5 ppb were detected in the drainage ditch water samples. All residues greater than 0.5 ppb were confirmed by using the Hall detector in the halogen mode. Residues of dicamba never exceeded 0.5 ppb, although trace amounts were observed late in the spray season. However, not even trace amounts of either of the soil incorporated herbicides (trifluralin and triallate) were detected in any of the return flow water samples throughout the irrigation season. For this reason, neither trifluralin nor triallate residues have been included in Table III.

In summary, the method presented can be used to determine both neutral and acidic herbicides in water with excellent reproducibility between analysts. The method employed diazomethane esterification of the acidic herbicides which is much less time consuming than using either pentafluorobenzyl bromide (Chau and Terry, 1976) or 2-chloroethanol/boron trifluoride (Chau and Terry, 1975). Low background interferences in natural waters easily permitted the limits of detection initially achieved with distilled water. When herbicide residues were present in the return flow water samples, the method showed good reproducibility between duplicate water samples, and these residues could be readily confirmed by using a specific gas chromatographic detector.

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Registry No. Dicamba, 1918-00-9; MCPA, 94-74-6; bromoxynil, 1689-84-5; 2,4-D, 94-75-7; picloram, 1918-02-1; triallate, 2303-17-5; trifluralin, 1582-09-8; water, 7732-18-5.

LITERATURE CITED

Agemian, H.; Chau, A. S. Y. *J. Assoc. Off. Anal. Chem.* **1977**, *60*, 1070–1076.
Bailey, G. W.; Thruston, A. D., Jr.; Pope, J. D.; Cochrane, D. R. *Weed Sci.* **1970**, 18, 413–419.
Chau, A. S. Y.; Terry, K. *J. Assoc. Off. Anal. Chem.* **1975**, *58*, 1294–1301.
Chau, A. S. Y.; Terry, K. *J. Assoc. Off. Anal. Chem.* **1976**, *59*, 633–636.
Grover, R. *Weed Res.* **1973**, *13*, 51–58.
Lee, H.; Chau, A. S. Y. *J. Assoc. Off. Anal. Chem.* **1983**, *66*, 651–658.
Rodgers, C. A.; Stalling, D. L. *Weed Sci.* **1972**, *20*, 101–105.
Smith, A. E. *Weed Res.* **1972**, *12*, 364–372.
Smith, A. E. *Weed Res.* **1976**, *16*, 19–22.
Smith, A. E.; Hayden, B. J. *Bull. Environ. Contam. Toxicol.* **1980**, *25*, 369–373.
Zepp, R. G.; Wolfe, N. L.; Gordon, J. A.; Baughman, G. L. *Environ. Sci. Technol.* **1975**, *9*, 1144–1150.

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