A Method for the Routine Semiquantitative Determination of Hydroxy-s-triazines in Soils

Derek C. G. Muir*[1] and Bruce E. Baker

A method is described for the routine, semiquantitative determination of several nonvolatile degradation products of the triazine herbicides atrazine, cyanazine, and cyprazine in soil samples. The procedure involves the extraction of soil samples with aqueous methanol and with a methanol–hydrochloric acid mixture and the partition of the chloro-s-triazines into ethyl acetate. The aqueous extract which contained the hydroxy-s-triazines was cleaned up by use of a column of cationic exchange resin; the hydroxy-s-triazines were converted to their methoxy derivatives by methylation with diazomethane. Gas chromatographic analysis was carried out by use of a Hall electrolytic conductivity detector (nitrogen mode). Recovery studies indicated that hydroxy-atrazine [2-hydroxy-4-(ethylamino)-6-(isopropyl-amino)-s-triazine], hydroxy-cyprazine [2-hydroxy-4-(cyclopropylamino)-6-(isopropylamino)-s-triazine], and cyanazine III [2-chloro-4-(1-carboxy-1-methylethylamino)-6-(ethylamino)-s-triazine] could be extracted relatively more efficiently from fortified (37.8–790.0 μg/kg) soil samples than could N-de-alkylated hydroxy-s-triazines. Overall recoveries of the hydroxy-s-triazines from soil were reduced by the poor efficiency of methylation to the corresponding methoxy-s-triazines.

The hydroxy-s-triazines are the major degradation products of the chloro-s-triazine herbicides in soil. The determination of the hydroxy degradation products is made difficult by their low solubility in nonacid or non-alkaline solvent systems (Ward and Weber, 1968), strong adsorption to organic matter and clay surfaces of soils (Weber, 1972), and low efficiency of derivatization for gas chromatographic analysis (Cochrane, 1975).

A variety of solvent systems have been used for the extraction of radiolabeled hydroxy-s-triazines from soil. These include sodium hydroxide solutions (Harris, 1967), hydrochloric acid (0.1 N)(Hance and Chesters, 1970), and glacial acetic acid (Best and Weber, 1974). The use of such extraction solvents requires that the chloro-s-triazines be extracted from the sample beforehand since these compounds would be expected to undergo partial hydrolysis under these conditions of extraction (Jordan et al., 1970).

Several authors have extracted hydroxy-s-triazines from soil by use of solvent systems that were considered unlikely to lead to hydrolysis of chloro-s-triazines. Flint and Aue (1970) extracted hydroxy-simazine [2-hydroxy-4,6-bis-(ethylamino)-s-triazine] from soil by ultrasonic stirring in acetonitrile–water–concentrated ammonia (86:10:4). Wright (1973) recovered cyanazine IV [2-hydroxy-4-(1-carboxy-1-methylethylamino)-6-(ethylamino)-s-triazine] from soil by extraction with hot water. Goswami and Green (1973) extracted atrazine [2-chloro-4-(ethyl-amino)-6-(isopropylamino)-s-triazine], ametryne [2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine], and hydroxy-atrazine [2-hydroxy-4-(ethylamino)-6-(iso-propylamino)-s-triazine] from soils with acidic methanol (pH 2.0). They reported recoveries of hydroxy-atrazine from Hawaiian soils that ranged from 80–90% but much lower recoveries (33%) from a montmorillonite clay. Khan et al. (1975) extracted atrazine and hydroxy-atrazine from spiked soil samples with methanol (solvent:soil ratio, 20:1). The extract was cleaned up on acidic alumina and the hydroxy-atrazine was determined by gas chromatography

(GLC) after methylation. They reported recoveries of hydroxy-atrazine of about 70%.

Khan (1975) and Cochrane (1975) reviewed the procedures for the derivatization of herbicide residues for GLC analysis. They noted that the methylation, silylation, or chlorination of hydroxy-s-triazines did not give high yields because of tautomerization of the proton of the hydroxy group with the nitrogen on the triazine ring. Lau et al. (1973) determined cyanazine IV by gas chromatographic analysis of its TCMS (3-trichloromethylthio-5,5-dimethylhydantoin) derivative. This method is not applicable, however, to the hydroxy-s-triazines that do not have the carboxylic acid group. Eberle and Gerber (1976) have reported the detection of hydroxy-atrazine in soil extracts, without prior derivatization, by high-pressure liquid chromatography with UV detection.

In the present investigation a method is evaluated for the extraction, cleanup, and gas chromatographic determination of several nonvolatile degradation products of chloro-s-triazine herbicides in soil. The procedure was designed to be used for the routine analysis of hydroxy-s-triazines in soils from fields that had been sprayed with triazine herbicides.

MATERIALS AND METHODS

Analytical Standards. Hydroxy-cyprazine [2-hydroxy-4-(cyclopropylamino)-6-(isopropylamino)-s-tri-azine] and N-deethylated hydroxy-atrazine [2-hydroxy-4-amino-6-(isopropylamino)-s-triazine] were obtained from Gulf Oil Chemicals. Cyanazine II [2-chloro-4-(1-carba-moyl-1-methylethylamino)-6-(ethylamino)-s-triazine], cyanazine III [2-chloro-4-(1-carboxyl-1-methylethyl-amino)-6-(ethylamino)-s-triazine], and cyanazine IV were obtained from Shell Research Ltd. N-Deisopropylated hydroxy-atrazine [2-hydroxy-4-amino-6-(ethylamino)-s-triazine] and ammeline [2-hydroxy-4,6-diamino-s-triazine] were obtained from Ciba-Geigy Ltd. Hydroxy-atrazine was synthesized in the laboratory from cyanuric chloride, ethylamine, and isopropylamine by a procedure described by Riden (1973). [14C]Hydroxy-atrazine (sp act., 0.72 μCi/mg) was synthesized from ring-labeled cyanuric chloride (New England Nuclear, Boston) by a procedure identical with that used for the synthesis of the unlabeled material.

The following methoxy-s-triazines were synthesized in the laboratory by methylation of their hydroxy analogues

Department of Agricultural Chemistry and Physics, Macdonald College of McGill University, Ste. Anne-de-Bellevue, Quebec, Canada H0A 1C0.

[1]Present address: Department of Fisheries and the Environment, Freshwater Institute, Winnipeg, Manitoba, Canada R3T 2N6.

SOIL
(Non-airdried; 100-150 g)

Shaking (1 hr)(MeOH: water, 2:1)(stand 16 h)

Blend Soil Residuum
(5 min.) (MeOH: 0.01NHCl, 1:1)

Soil residuum
discarded → Aqueous Methanol

Evaporation of MeOH

Partition with ethylacetate
pH 9.0

Aqueous phase

Evaporate
to 5 ml volume

Cleanup on resin
column (AG 50W x 8)

Methylation with
Diazomethane

GLC of hydroxy-s-triazines
as their methoxy-derivatives

Organic phase
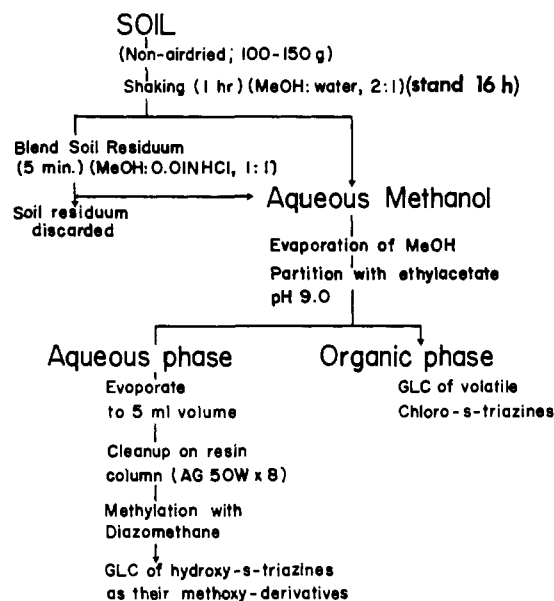
GLC of volatile
Chloro-s-triazines

Figure 1. Outline of the soil extraction procedure.

with diazomethane: N-deisopropylated atratone [2-amino-4-(ethylamino)-6-(methoxy)-s-triazine], methylated cyanazine IV (MCIV) [2-(1-methylcarboxyl-1-methylethylamino)-4-(ethylamino)-6-(methoxy)-s-triazine], and methylated cyanazine III (MCIII) [2-chloro-4-(1-methylcarboxy-1-methylethylamino)-6-(ethylamino)-s-triazine]. The following methoxy-s-triazines were also synthesized from the corresponding chloro-s-triazines by methoxylation (sodium methoxide): atratone [2-amino-4-(isopropylamino)-6-(methoxy)-s-triazine], cypratone [2-(isopropylamino)-4-(cyclopropylamino)-6-(methoxy)-s-triazine], and 2,4-diamino-6-(methoxy)-s-triazine. The purity of the methoxy derivatives was found to be greater than 95% on the basis of a comparison of their gas chromatographic responses with those of the corresponding chloro-s-triazines. The identity of each methoxy-s-triazine derivative was confirmed by mass spectrometry.

Soil Extraction and Clean-Up Procedure. The analytical procedure was based on the methods of Sirons et al. (1973), Wright (1973), Purkayastha and Cochrane (1973), and Goswami and Green (1973). The clean-up procedure for the sample extracts was based on the method of Lau et al. (1973). The procedure is outlined in Figure 1.

Soil samples (nonair-dried; 150 g of wet weight) were placed in jars (1.7 L with screw caps). Methanol-water (2:1) (400 mL) was added, and the jars were shaken for 1 h at high speed (Eberbach mechanical shaker). The samples were allowed to stand overnight and were shaken for an additional 20 min the following day. The mixture was transferred quantitatively to a Büchner funnel with the aid of aqueous methanol. After filtration the soil residuum was transferred to a blender (Waring) jar and blended (5 min) with methanol-0.01 N hydrocloric acid (1:1) (175 mL). The mixture was filtered, and the combined extracts were neutralized with dilute NaOH and concentrated (rotary evaporator, 50 °C) to a volume of 50-70 mL. The aqueous phase was transferred to a separatory funnel with distilled water to give a total volume of 100 mL. It was adjusted to pH 9 (dilute NH₄OH) for soils containing atrazine residues, or to pH 4 (dilute HCl) for soils that had been sprayed with cyanazine, and then partitioned with ethyl acetate (2 × 100 mL). The organic phase was retained for determination of chloro-s-triazines. The aqueous phase was concentrated (rotary evaporator,

Table I. Retention Times and Responses of Triazine Compounds on a Carbowax 20M + OV-17 Column with the Hall ECD

Compounds	Retention time, min	Response,[a] ng, ¹/₂ f.s.d.
Atrazine	3.80	2.0
Atratone	3.20	1.8
Cypratone	5.60	2.6
N-Deethylated atratone	4.12	2.2
N-Deisopropylated atratone	7.05	2.9
2,4-Diamino-6-methoxy-s-triazine	10.60	10.8
MCIV[b]	11.20	2.0
MCIII[c]	12.35	2.8

[a] Response of the Hall ECD in nanograms (ng) for 50% of full-scale recorder deflection (f.s.d.) at attenuation setting of 1. [b] Methylated cyanazine IV.
[c] Methylated cyanazine III.

55 °C) to a small volume (3-5 mL).

Cleanup of the aqueous phase was accomplished on a column of strongly acid cationic exchange resin. The resin (AG 50W × 4; 80-100 mesh) (BioRad Laboratories Ltd., Richmond, Calif.) was slurried with deionized water and poured into a glass tube (30 × 1 cm with Teflon stopcock) to give a column of 10 × 1 cm. The column was topped with sand (1 cm). The sample extract was neutralized and transferred quantitatively to the column with water (3-5 mL). The column was washed with 20 mL of water followed by a mixture of methanol and 3 N NH₄OH (2:1) (15 mL) at an elution rate of 1 to 2 mL/min. The water and the first 10 mL of the methanol eluate were discarded. The remaining 5 mL of methanolic eluate, which contained hydroxy-s-triazines, was collected. The column was washed with an additional 10 mL of ammoniacal methanol (methanol-3 N NH₄OH, 1:1). The combined eluates were evaporated to dryness with the aid of a stream of nitrogen.

Derivatization. The cleaned-up extract was dissolved in methanol (0.5 to 1.0 mL) and was methylated (60 °C, 1 h) by use of an excess of diazomethane (20 mg of diazomethane/mL of diethyl ether; 3-4 mL), as described by Khan et al. (1975), in a screw-capped test tube. The reaction mixture was cooled and the ethereal solution evaporated just to dryness. The residue was dissolved in methanol for gas chromatographic analysis.

Gas Chromatography. All gas chromatography was performed on a Tracor 550 GC equipped with a Hall electrolytic conductivity detector (Hall ECD). Injection port, column outlet, and vent valve (Valco, 4 port) temperatures were 225, 250, and 250 °C, respectively.

The methoxy-s-triazines were separated on a column (1.8 m × 0.6 cm o.d. glass) consisting of 1.5 m of 5% Carbowax 20M followed by 0.3 m of 5% OV-17, both on Gas-Chrom Q (80-100 mesh), at 195 °C. MCIII and MCIV were separated on a column (0.7 m × 0.6 cm o.d. glass) of 1.5% CHDMS on Gas-Chrom Q (80-100 mesh) at 180 °C or on the Carbowax 20M + OV-17 column (195 °C). Retention times and responses of the methoxy-s-triazines on the 1.8 m column are given in Table I.

Operating conditions for the Hall ECD were as follows: solvent, isopropanol-water (30:70); solvent flow rate, 0.4-0.5 mL/min; furnace temperature, 900 °C; reaction gas (H₂), 20 mL/min; resin bed, two cartridges (7 cm × 2 cm) of Duolite ARM 381 (20-50 mesh); reaction tube (quartz), 2.8 mm o.d. × 1.5 mm i.d. × 15 cm with two strands (5 cm) of nickel wire and 1 cm of strontium hydroxide scrubber.

Recovery Studies. Known quantities of [¹⁴C]-hydroxy-atrazine as well as unlabeled hydroxy-cyprazine, cyanazine III, N-deethylated hydroxy-atrazine, N-deisopropylated hydroxy-atrazine, and ammeline were added

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Table II. Some Physical Characteristics of the Soils Used in the Recovery Experiments

Soil no.	Clay, %	Silt, %	Sand, %	pH[a]	Moisture,[b] %	Organic matter, %
1	9.2	9.7	81.1	4.70	1.8	3.64
2	23.4	15.9	60.7	4.65	4.8	1.75
3	8.3	18.3	73.4	6.50	12.7	4.70

[a] In 0.02 M $CaCl_2$. [b] Moisture content of air-dried soil.

Table III. Average Recovery of Hydroxy-s-triazines and Cyanazine III from Soil

Compound	Concn, ppb	Av recov,[a] %	Standard error, %
Hydroxy-atrazine[b]	790.0	67.5	2.7
	67.5	63.4	5.8
Hydroxy-cyprazine	442.5	46.1	9.4
	37.8	37.3	12.1
Cyanazine III[c]	554.3	65.0	9.0
	47.4	49.5	20.6
N-Deethylated hydroxy-atrazine	416.0	41.0	8.3
	35.5	31.1	14.8
N-Deisopropylated hydroxy-atrazine	421.8	34.8	7.0
	36.0	18.2	7.4
Ammeline	394.0	7.4	1.1
	33.6	6.2	5.1

[a] Average of 18 analyses at each concentration. [b] ^{14}C-labeled compound. Determined by liquid scintillation counting. [c] Cyanazine III was partitioned into ethyl acetate at pH 4.0.

(methanol solution) to samples of three different soils. The soils (air-dried and ground to pass through a 2-mm seive) were chosen on the basis of differences in physical characteristics (Table II) and were similar to soils on which the chloro-s-triazines were applied in field experiments (Muir and Baker, 1976). The fortified soil samples were mixed by end-over-end tumbling (10 h), and water was added to bring the soil samples to their approximate field moisture capacity (20% by weight). The soils were held at room temperature (20-25 °C) until they were analyzed. Unfortified soil samples, treated identically, were used as blanks.

The fortified soil samples were subsampled (in triplicate) after 5 and 21 days and analyzed as described previously. [^{14}C]Hydroxy-atrazine was determined by liquid scintillation counting of aliquots of the cleaned-up extracts using a Packard Model 3003 liquid scintillation counter. Sample extracts (0.5 mL) were dissolved in 10 mL of "Aquasol" (New England Nuclear) and counted twice (10 min). Counting efficiencies were determined by use of an external standard technique.

RESULTS AND DISCUSSION

The average recoveries of [^{14}C]hydroxy-atrazine, cyanazine III, and the nonradiolabeled hydroxy-s-triazines at two levels of fortification (three soil types and two times

of analysis at each concentration) are given in Table III.

The recovery of [^{14}C]hydroxy-atrazine is similar to that reported by Skipper and Volk (1972) who used methanol (Soxhlet) as extraction solvent. Khan et al. (1975) reported recoveries of unlabeled hydroxy-atrazine after column cleanup and methylation that were similar to those found in the present study. The recovery efficiency of hydroxy-atrazine is higher than that reported by Goswami and Green (1973) for the extraction of hydroxy-atrazine from a calcium-saturated montmorillonite clay. The recoveries of hydroxy-atrazine are lower, however, than those reported by several authors who used relatively strong acid conditions (Hance and Chesters, 1970; Best and Weber, 1974).

The two concentrations of the hydroxy-s-triazines and cyanazine III listed in Table III were intended to approximate the upper and lower range of concentration of these compounds in field soils. Statistical analysis (Student's t-test on paired observations at each concentration) showed that there were no significant differences in recovery efficiencies at each concentration despite tenfold differences in the level of fortification. The results were consistent with the findings of other workers who used similar ranges of concentration of chloro-s-triazines in fortified soil samples (Ramsteiner et al., 1974; Beynon, 1972; Mattson et al., 1970).

The recoveries of the individual hydroxy-s-triazines at each extraction time (5 and 21 days after fortification) were compared statistically by use of a factorial design with the factors of compounds, soils, and concentrations "nested" in compounds. The homogeneity of the variances within the group of hydroxy compounds was verified by use of Bartlett's test (Steel and Torrie, 1960). Significant differences in recovery of the compounds were then evaluated by use of Duncan's test (Table IV).

The results (Table IV) indicate that there were no significant differences (5% level of probability) between the recovery of hydroxy-atrazine and cyanazine III at the two extraction times. Recoveries of hydroxy-cyprazine and N-deethylated hydroxy-atrazine were significantly lower than that of hydroxy-atrazine. The higher recovery of [^{14}C]hydroxy-atrazine reflects the fact that it was not necessary to methylate this compound before its determination by scintillation counting. Cyanazine III, a chloro-s-triazine, had a higher recovery because of the high efficiency of methylation of the carboxylic acid group. The recoveries of ammeline were significantly lower than those of the other hydroxy-s-triazines.

In general, the recoveries of the hydroxy-s-triazines decreased with the extent of N-dealkylation. This effect has also been reported for chloro-s-triazines (Sirons et al., 1973; Beynon, 1972). The N-dealkylated hydroxy-s-triazines might be expected to be strongly bound to soil surfaces due to their primary amino groups. It is apparent from these results that more rigorous extraction conditions are necessary for the recovery of the N-dealkylated hydroxy compounds from soil. Strongly acid or alkaline

Table IV. Comparison of the Mean Recoveries of Hydroxy-s-triazines and Cyanazine III Using Duncan's Test

Extraction time, days	Standard error, %	Mean recoveries of ranked[a] compounds[b]					
		HA	III	HC	DEHA	DIHA	Ammel
5	4.0	68.2	56.5	48.5	43.5	31.0	9.0
21	2.8	62.7	58.4	34.8	30.2	22.1	4.4

[a] The compounds are ranked in order of decreasing percentage recovery. Any two means underscored by the same line are not significantly different at the 5% level of significance. [b] HA, hydroxy-atrazine; III, cyanazine III; HC, hydroxy-cyprazine; DEHA, N-deethylated hydroxy-atrazine; DIHA, N-deisopropylated hydroxy-atrazine; Ammel, ammeline.

Table V. Recovery of Triazine Compounds from
Cationic Exchange Resin Columns

Compound	Quantity added, μg	Av recov,[a] %	Standard error, %
Atrazine	5.2	95.0	2.6
Cyprazine	10.0	93.5	3.0
N-Deethylated atrazine	13.5	90.2	5.2
N-Deisopropylated atrazine	14.0	88.1	6.3
Cyanazine II	19.4	10.0	7.1
Cyanazine III	22.2	0.0	
Hydroxy-atrazine[b]	16.0	90.5	1.5
	8.0	89.6	1.5
Cyanazine IV	25.1	88.4[c]	3.4
	50.2	87.0[c]	5.3

[a] Average of three determinations. [b] ^{14}C-labeled; determined by liquid scintillation counting. [c] Corrected for an average methylating efficiency of 57%.

conditions need to be avoided in the initial extraction of the soil since chloro-s-triazines, especially cyanazine (Brown et al., 1972), could hydrolyze to their corresponding hydroxy derivatives. In the reextraction step (see Figure 1) prolonged use of strong acid or alkali could hydrolyze the unextracted portion of the chloro-s-triazines in the soil residuum. Sirons (1977) cleaned up fish extracts containing atrazine by use of a brief extraction into 0.5 N HCl. A brief treatment (blending or shaking) of the soil residuum with strong acid might be a useful approach for the recovery of the more polar triazine compounds but this was not investigated in the present work.

Neither time of incubation nor soil type had significant effects on the efficiency of extraction of most hydroxy-s-triazines from soils. Best and Weber (1974) noted that the low biological availability of hydroxy-atrazine resulted in an almost negligible conversion of this compound to other triazine derivatives over a 5-month incubation period. Goswami and Green (1973) have noted the effect of clays containing a high permanent negative charge on the reduction in the recovery of hydroxy-atrazine from soil. In the present work certain concentrations of hydroxy-atrazine, N-deisopropylated hydroxy-atrazine, and ammeline were found to have significantly (1% level of probability) lower recoveries with soil of higher clay content (Table II). The clay in all three soils was predominately of the illite type.

Significant differences in the recoveries of the hydroxy-s-triazines due to soil pH were not observed in the present study; the acidity of the sandy soils that were used may have contributed greatly, however, to the low overall recoveries. The soil pH levels were very similar to the pK_a values reported for several hydroxy-s-triazines (Weber, 1967). The hydroxy compounds would therefore be expected to be strongly adsorbed to clay and organic matter surfaces after 5 and 21 days of incubation. The results of the present study did not demonstrate that the organic matter content of the three soils had any significant effect on the recovery of hydroxy-s-triazines. Hayes (1970) has noted that the clay content of soils could have considerable influence on the adsorption of triazines in instances where the organic carbon contents of the soils were less than 5%. The somewhat lower recoveries of several of the hydroxy-s-triazines in soil 2 (Table II) may have resulted therefore from the combined effect of the high clay content and the organic matter.

The losses of hydroxy-s-triazines at each step in the determination were evaluated in order to determine the importance of soil extraction efficiency in the overall recovery of these compounds. Known quantities of analytical standards were added to sample blanks in the
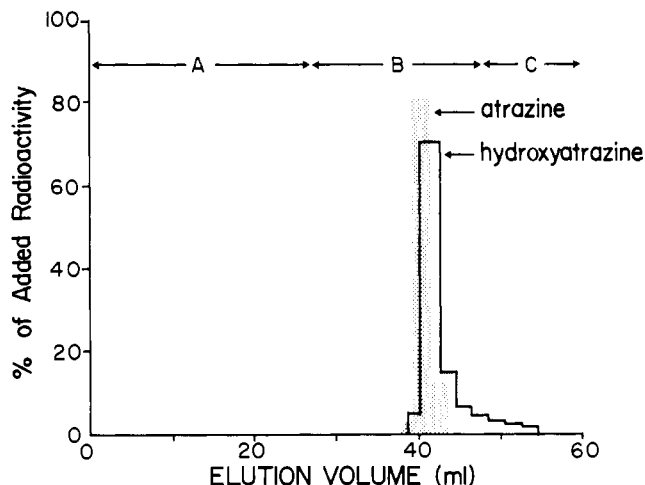

Figure 2. The pattern of elution of atrazine and [14C]hydroxy-atrazine from a column of cationic exchange resin: eluate A, water; eluate B, methanol–3 N NH₄OH (2:1); eluate C, methanol–3 N NH₄OH (1:1).

clean-up and derivatization steps.

The recoveries of several chloro-s-triazines and hydroxy-s-triazines after elution through the column of cationic exchange resin are shown in Table V. Relatively low losses of chloro-s-triazines were observed on the resin column, with the exception of cyanazine II and cyanazine III which were converted almost quantitatively to cyanazine IV. The short period of time during which the chloro-s-triazines were on the column may have served to reduce the degree to which the compounds were hydrolyzed. Larsen and Bakke (1975) reported that cleanup by use of strongly acid cationic exchange resin and also paper chromatography with acidic solvent systems caused hydolysis of chloro-s-triazines. This problem was avoided in the present work by the partition of the chloro-s-triazines into ethyl acetate. The N-dealkylated chloro-s-triazines, which are less efficiently partitioned from the aqueous phase (Sirons et al., 1973; Muir and Baker, 1976), might be expected on the basis of the results in Table V, to pass through the resin column without hydrolysis.

A comparison of the elution patterns (cationic exchange resin; AG 50W × 4) of [14C]hydroxy-atrazine and atrazine was made by fractionation of the column eluate. Figure 2 shows that atrazine and hydroxy-atrazine were eluted from the column with the same elution volume. The other hydroxy-s-triazines had similar elution volumes to that of hydroxy-atrazine with the methanol–ammonia eluates. The tailing of the hydroxy-atrazine peak suggests that a small portion of the triazine residue was strongly adsorbed to the resin.

Table VI shows the results of experiments on the methylation of hydroxy-s-triazines and cyanazine III by use of diazomethane. Cyanazine III and N-deethylated hydroxy-atrazine gave the highest yields of methylated derivatives whereas hydroxy-atrazine gave a relatively low yield. The presence of large amounts of soil coextractives (150 g sample) lowered the efficiency of methylation of hydroxy-atrazine (based on the partition of radioactivity into diethyl ether) by 5 to 10%.

Khan et al. (1975) noted that the methylation of hydroxy-atrazine with diazomethane could not be regarded as quantitative because of considerable variation in the yields of the methylated derivative. The results of Table VI indicate that there was considerable variation in the methylation efficiency of several other hydroxy-s-triazines. Chlorination (Schroeder et al., 1972) and silylation (Flint

Table VI. Efficiency of Methylation of
Hydroxy-s-triazine Using Diazomethane[a]

Compound	Quantity, μg	Repli-cates	Recov, %	Standard error, %
Hydroxy-atrazine	16.0	3	50.2	0.6
	8.5	4	56.0	4.5
	3.4	4	59.1	7.6
[14C]Hydroxy-atra-zine[b]	150.0	4	52.5	3.8
	30.0	3	51.5	2.9
	3.0	4	48.0	0.9
Hydroxy-cypra-zine	8.1	4	62.5	5.3
	4.1	4	63.7	12.0
N-Deethylated hydroxy-atrazine	28.6	4	73.4	17.2
	5.7	4	93.9	6.2
	2.9	4	90.9	9.3
N-Deisopropylated hydroxy-atrazine	9.7	4	70.4	3.1
Cyanazine IV	27.7	3	64.9	3.8
	12.6	3	49.9	9.2
Cyanazine III	44.4	3	91.0	11.8
	22.2	3	98.3	9.2
Ammeline	17.8	4	16.5	1.6
	8.9	4	18.7	3.5

[a] Results (%) are not corrected for differences in molecular weights of hydroxy and methylated derivatives.
[b] Partition into ether after methylation and counted by liquid scintillation counting in the presence of "coextractives".

and Aue, 1970) procedures for the derivatization of the hydroxy compounds were also investigated. The diazomethane methylation procedure was found to be more useful than chlorination or silyation because additional cleanup of the reaction mixture before GLC was unnecessary and single distinctive gas chromatographic peaks were produced for each methoxy derivative.

If the recovery efficiencies (Table III) are corrected for losses in the derivatization and clean-up steps, it is apparent that hydroxy-atrazine, hydroxy-cyprazine, and cyanazine III were extracted relatively well from soil (70–80%) while the N-dealkylated hydroxy-s-triazines were recovered with an efficiency of 40–50%. The procedure did permit the semiquantitative determination of several hydroxy-s-triazines in field soils (Muir and Baker, 1977) on a routine basis. The use of high-pressure liquid chromatography to avoid the necessity for the derivatization of hydroxy-s-triazines might make possible the quantitative determination of some of these compounds.

ACKNOWLEDGMENT

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