

the rice plant, is stored in the form of metabolites throughout the growth cycle, and is eventually translocated into the ripening grain. In our opinion, it is a more likely possibility that the DCA in the rice grains originates from soil-bound residues, and enters the plant during the formation and ripening of the grain.

Whether or not aniline residues derived from other phenylamide herbicides behave similarly to DCA is at this time largely a matter of conjecture. 4-Chloroaniline was mineralized at a slightly faster rate than DCA, but otherwise behaved in soil (Bartha, 1971) and in model reactions (Hsu and Bartha, 1974a) very similarly to DCA. Rice grains that were harvested in 1958 (before the introduction of propanil), and had a *N*-(3-chlorophenyl)-carbamate (chloroprotham) treatment history, contained 3-chloroaniline (Still and Mansager, 1969).

Whether or not soil-bound DCA and perhaps other similarly bound aniline residues constitute a source of crop contamination of practical importance remains to be established by future experimental work. We do not wish to imply that such a hazard was conclusively demonstrated here. Nevertheless, it is hard to conclude from the presented evidence that soil-bound DCA residues can be ignored safely. Our present inability to reliably monitor the humic complexes of DCA and of perhaps other chloroanilines is a highly unsatisfactory state of affairs. A more general awareness of this analytical challenge will hopefully hasten the development of a suitable procedure.

ACKNOWLEDGMENT

We are grateful to S. P. Mathur for the *A. versicolor* culture.

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Received for review January 14, 1975. Accepted September 3, 1975. The work described in this paper of the Journal Series, New Jersey Agricultural Experiment Station, New Brunswick, N.J., was supported by Regional Research Fund NE-53.

Detection of Triazine Herbicides and Their Degradation Products in Tile-Drain Water from Fields under Intensive Corn (Maize) Production

Derek C. Muir* and Bruce E. Baker

The herbicides cyanazine, cyprazine, atrazine, and metribuzin were applied (post-emergence) to plots which were drained by separate tile drains (depth 1.2-1.6 m). Water samples were collected from the tile outlets and extracted with ethyl acetate. In the first season of monitoring, herbicide concentrations ranged from 0.30 to 1.49 $\mu\text{g}/\text{l}$. for atrazine, from 0.00 to 0.68 $\mu\text{g}/\text{l}$. for cyanazine, and from 0.00 to 0.57 $\mu\text{g}/\text{l}$. for cyprazine. Similar levels of the chloro-*s*-triazine herbicides were found in the tile-drain water during the second year of the study. Metribuzin, which was applied during the second year, was found in the tile-drain water in concentrations ranging from 0.00 to 1.65 $\mu\text{g}/\text{l}$. The metabolites deethylated atrazine (2-chloro-4-isopropylamino-6-amino-*s*-triazine) and cyanazine amide [2-chloro-4-(1-carbamoyl-1-methylethylamino)-6-ethylamino-*s*-triazine] and deisopropylated atrazine (2-chloro-4-amino-6-ethylamino-*s*-triazine) were detected at concentrations which were similar to those of the parent compounds. The discharge (grams/hectare) of herbicide residues in the tile-drain water was determined over a 9-month period.

There are relatively few published reports on field studies of herbicide residues in ground water despite the widespread use of these chemicals. Wheeler and Mansell (1974) found that Terbacil and 2,4-D were detected (10 to 110 $\mu\text{g}/\text{l}$.) in subsurface drainage water collected from a citrus grove under irrigation. Mackenzie and Vjsets (1974)

have discussed the question of insecticide residues in tile-drain water and have pointed out there is a scarcity of information on the fate of herbicides in drainage water.

Sirons et al. (1973) reported on the persistence in soil of the major phytotoxic degradation products of atrazine and cyanazine. Their findings indicate that relatively large quantities of deethylated atrazine and deisopropylated atrazine are present in the upper 6 cm of the soil profile. Beynon et al. (1972) reported that the levels of cyanazine amide (0-10 cm depth) were double those of the parent compound 4 weeks after application of the herbicide.

*Department of Agricultural Chemistry, Macdonald College of McGill University, Macdonald College, Quebec, Canada HOA 1C0.

Table I. Description of Experimental Area under Corn Production (1973, 1974)

Field and drain no.	Area of field, ha	Tile drain depth, m	Tile drain slope, %	Soil		Herbicide treatment
				Series name	Taxonomic name	
1	1.75	1.20	0.25	Courval sandy loam	Aquic humic cryorthod	Atrazine (Atrax 90W), ^a 2.80 kg/ha
2	1.16	1.32	0.18	Ste. Damase light sandy loam	Aquic humic cryorthod	Cyprazine (Outfox), ^b 1.12 kg/ha
3	1.30	1.63	0.20	Ste. Damase light sandy loam	Aquic humic cryorthod	Cyanazine (Bladex 80W), ^c 3.36 kg/ha
4	0.60	1.15	0.35	Rideau clay and Ste. Amable loamy sand	Humaquept and aquic humic cryorthod	Metribuzin (Lexone), ^d 0.56 kg/ha

^a Ciba-Geigy Canada Ltd. ^b Gulf Chemicals Canada Ltd. ^c Shell Chemical Co. ^d DuPont Chemicals Canada Ltd.

These studies suggest that the upper layer of the soil contains relatively large amounts of triazine degradation products which can subsequently move to lower levels in the soil and presumably into tile-drain water.

The present study on the herbicide content of tile-drain water is part of an investigation on the persistence of the degradation products of triazine herbicides in the soil of fields used for corn (*Zea mays* L.) production. Water samples were taken during the months following spray application in order to determine the quantity of triazine herbicides and their degradation products that were leaching into the subsurface drainage systems.

The triazine herbicides atrazine, cyprazine, and cyanazine were chosen for the study because of their widespread use in southern Quebec for selective weed control. The triazinone metribuzin, which was recently introduced in this region for the control of broadleaf weeds and grasses in soybeans, was included in the second year of the study.

MATERIALS AND METHODS

Field Experiment. A 5 ha area which is located on the Macdonald College farm was used in the present investigation. The four fields which comprise the experimental area are drained by four separate tile-drain lines (10-cm diameter). Pertinent information concerning these fields and the spray treatments are given in Table I. Water samples were taken from the overflow on a V-notch weir which is located in a manhole at the tile-drain outlet. Flow rate measurements were made continuously using a float and a level recorder located in the manhole above the weir (Iqbal, 1972). The manholes were located in a grassy area approximately 4 m from the edges of the fields and were covered at all times. The water samples were collected in glass jars (1.7 l.) and were stored at 4°C until they were analyzed. In 1973, water samples were taken 14 days before and 2, 3, 6, 9, 14, 21, 28, and 40 days after the herbicide application. The tile drains were dry throughout the months of August and September; sampling was not resumed until the following April (10 months after the herbicide application). In 1974 the fields were again treated with herbicide. Sampling continued throughout the months of June, July, November, and December.

Analytical Procedure. *Gas Chromatography.* Analytical standards of the herbicides and their degradation products were obtained from Ciba-Geigy Agricultural Chemicals, Shell Research Ltd., DuPont Canada Ltd., and Gulf Research Ltd.

Analyses of the extracts of the water samples were made using a Varian 1400 GC equipped with an alkali-flame detector. The gas flow rates and detector cap were those recommended by Osadchuk (1972). The following GLC columns were used: (a) 2 m × 4 mm (i.d.) Pyrex tube packed with 6% Carbowax 20M on Chromosorb W-HP and operated at 200°C; (b) 0.5 m × 4 mm (i.d.) Pyrex tube

packed with 1.5% CHDMS on Chromosorb W-HP and operated at 220°C; (c) 0.5 m × 4 mm (i.d.) Pyrex tube packed with 5% Silar 5 CP on Chromosorb W-HP and operated at 195°C. Detector oven and injection port oven temperatures were 245 and 220°C, respectively.

Many of the results were confirmed using a Hall Electrolytic Conductivity Detector (nitrogen mode) attached to an F and M Model 810 GC oven by means of a 22 cm Pyrex tube (6 mm o.d. × 0.5 mm i.d.). The detector was operated under the following conditions: transfer line, 225°C; pyrolysis furnace, 860°C; solvent system, 30% 2-propanol in water; helium, 60 ml/min; hydrogen, 40 ml/min; vent valve temperature, 200°C. The GLC columns and operating temperatures were the same as those used with the alkali flame detector.

Extraction. The water samples were extracted with ethyl acetate (Beynon, 1972) using a vortex stirring procedure (Ripley et al., 1974). The water sample was transferred to an erlenmeyer flask (2 l.) and ethyl acetate was added to give a solvent-water ratio of 1:6. The mixture was stirred for 45 min and the phases were separated by means of a separatory funnel. The extraction was repeated two more times with a solvent-water ratio of 1:20. The extracts were combined, dried over anhydrous sodium sulfate, and then concentrated to small volume for gas chromatographic analysis.

RESULTS AND DISCUSSION

Recovery Experiments. Samples of the tile-drain water were spiked with the three herbicides and several of their degradation products and were allowed to stand 24 hr before extraction. Since the tile-drain samples varied between pH 7.5 and 8.5, the spiked samples were adjusted to different pH values in order to determine whether or not pH affects recovery. The results of the experiment are reported in Table II. Recoveries ranged from 40.0% (cyanazine amide) to 113% (deethylated cyanazine). It would appear that lower pH values might lead to somewhat higher recoveries from the tile-drain water, as far as atrazine, cyprazine, deethylated atrazine, and deisopropylated atrazine are concerned. It has been reported (Ward and Weber, 1968), however, that the aqueous solubility of most triazine herbicides does not vary appreciably between pH 5.0 and 10.0.

Drain-Water Analysis. Table III gives the results of the analyses of the water samples as well as the tile-drain flow rates on each sampling day. Atrazine and its degradation products were found in the water from the four tile drains several days before pesticide application. This was to be expected in view of the fact that there had been a yearly application of this pesticide since 1968. The levels of deisopropylated atrazine were near the detection limit (0.01 µg/l.) before the application of atrazine and cyanazine but increased to 0.10 and 0.19 µg/l. for tile drains no. 1

Table II. Recovery of Triazine Herbicides and Degradation Products from Spiked Samples of Tile-Drain Water

Compound	Amount added, $\mu\text{g/l.}$	Extraction conditions ^a (solvent/water ratio)	pH	Av recovery, %
Atrazine	7.00	1:5	7.0	97.0 (3) ^b
	7.00	1:5	9.0	92.0 (3)
	3.44	1:6	7.5	94.4 (2)
	0.69	1:6	7.5	93.7 (2)
Cyprazine	9.93	1:5	7.0	100.5 (3)
	9.93	1:5	9.0	92.0 (3)
	6.68	1:6	7.5	99.8 (2)
	1.34	1:6	7.5	93.7 (2)
Deethylated atrazine	5.40	1:5	7.0	101.2 (3)
	5.40	1:5	9.0	92.7 (3)
	5.40	1:6	7.5	94.1 (2)
Deisopropylated atrazine	1.08	1:6	7.5	95.3 (2)
	9.54	1:5	7.0	94.3 (3)
	9.54	1:5	9.0	80.3 (3)
Cyanazine	1.28	1:6	7.5	83.0 (3)
	13.00	1:5	8.0	99.5 (2)
	8.90	1:6	7.5	93.7 (3)
Cyanazine amide	58.80	1:5	8.0	76.1 (2)
	19.40	1:6	7.5	40.0 (3)
Deethylated cyanazine	12.50	1:5	8.0	113.0 (2)
	9.17	1:6	7.5	90.8 (3)
Metribuzin	9.83	1:6	7.5	91.1 (3)
	2.45	1:6	7.5	97.2 (3)

^a The ratios reported here are for the first extractions. This was followed by two subsequent extractions in which the solvent/water ratio was 1:20. ^b Number of replicates.

Table III. Concentrations of Herbicides and Their Degradation Products in Tile-Drain Water for a Given Tile-Drain Flow Rate

Sampling date	Triazine herbicides and degradation products, $\mu\text{g/l.}$												
	Tile drain no. 1				Tile drain no. 2			Tile drain no. 3			Tile drain no. 4		
	Q ^a	Atrazine	DEA ^b	DIA ^b	Q ^a	Cyprazine	DEA ^b	Q ^a	Cyanazine	CA ^b	DIA ^b	Q ^a	Metribuzin
26/5/73	0.88	0.33	0.70	0.03	0.25	<0.01	0.80	0.49	<0.01	<0.04	0.03		
(6/6/73) ^c	0.91				0.57			0.93					
8/6/73	0.54	0.29	0.60	0.03	0.42	<0.01	0.57	0.39	<0.01	<0.04	0.05		
9/6/73	0.54	0.24	0.56	0.04	0.37	<0.01	0.67	0.20	<0.01	<0.04	0.06		
12/6/73	2.26	1.49	0.40	0.01	1.46	0.57	1.42	2.45	0.29	0.15	0.02		
15/6/73	1.28	0.62	0.85	0.11	0.94	0.25	0.85	0.72	0.36	0.35	0.04		
20/6/73	1.10	0.63	1.11	0.08	0.79	0.29	0.96	0.59	0.68	3.30	0.11		
27/6/73	0.72	0.52	0.82	0.07	0.13	0.27	0.99	0.13	0.17	2.00	0.09		
4/7/73	0.60	0.40	1.08	0.10	0.06	0.32	0.52	0.08	0.11	0.66	0.19		
18/7/73	0.10	0.32	0.90	0.03	d	d	d	d	d	d	d		
10/8/73	d	d	d	d	d	d	d	d	d	d	d		
8/9/73	d	d	d	d	d	d	d	d	d	d	d		
5/5/74	6.00	0.51	0.36	0.01	4.00	<0.01	0.15	2.80	<0.01	<0.04	0.11		
15/4/74	4.10	0.23	0.57	0.03	2.64	<0.01	0.20	2.78	<0.01	<0.04	0.05		
29/4/74	3.41	0.13	0.67	0.04	2.51	<0.01	0.24	2.57	<0.01	<0.04	0.18		
13/5/74	4.58	0.21	1.16	0.02	3.72	0.04	0.33	3.20	<0.01	0.14	0.22		
3/6/74	0.50	0.12	0.58	0.02	0.37	0.03	0.23	0.35	<0.01	<0.04	0.55	0.09	<0.01
(12/6/74) ^c	0.80				0.31			0.35			0.09		
20/6/74	0.40	0.06	0.47	0.02	0.22	0.51	0.33	0.17	<0.01	0.21	0.26	0.06	<0.01
1/7/74	0.35	0.15	0.77	0.02	0.04	0.76	0.69	0.17	<0.01	0.26	0.35	0.18	0.46
10/7/74	1.56	1.09	1.10	0.04	0.35	0.51	1.00	0.30	0.43	0.27	0.23	0.11	0.02
19/7/74	0.20	0.82	0.74	0.06	d	d	d	0.09	0.48	0.43	0.40	0.04	0.09
30/7/74	0.91	10.82	7.71	0.78	2.89	4.13	3.60	0.57	1.06	2.56	0.62	0.43	1.65
10/8/74	d	d	d	d	d	d	d	d	d	d	d	d	d
3/9/74	0.04	0.41	0.47	0.04	d	d	d	d	d	d	d	d	d
3/10/74	d	d	d	d	d	d	d	d	d	d	d	d	d
23/11/74	1.56	0.41	1.00	0.07	1.43	0.12	0.35	1.08	<0.01	0.13	0.10	0.43	<0.01
8/12/74	2.26	1.78	2.15	0.09	2.64	0.16	0.34	3.07	<0.01	0.31	0.02	0.56	<0.01
22/12/74	1.01	0.24	1.05	0.03	1.51	0.09	0.35	0.95	<0.01	0.11	0.02	0.09	<0.01

^a Q = millimeters per day. ^b DEA, deethylated atrazine; CA, cyanazine amide; DIA, deisopropylated atrazine. ^c Date of application of herbicide. ^d Tile-drain weir dry.

and no. 3, respectively, 4 weeks after the applications. Other workers have shown that deisopropylated atrazine is a soil microbial metabolite of cyanazine (Beynon et al., 1972; Sirons et al., 1973) as well as of atrazine.

The concentration of 2-chloro-4-isopropylamino-6-amino-s-triazine (decyclopropylated cyprazine; deethylated atrazine) in the water (1973) from tile drain no. 2 was consistently higher than that of cyprazine because of the

presence of deethylated atrazine residues in the soil resulting from the application of atrazine in previous years.

The early appearance (6 days after application) of cyprazine and cyanazine, neither of which had been used before in this area, the tile drains no. 2 and no. 3, respectively, was undoubtedly the result of heavy rainfall and the resultant high flow rates of drain water. It will be noted that similar concentrations of herbicides in the

Table IV. Loss through Tile-Drain Water, of Herbicides and Their Degradation Products from Fields under Corn Production (1974)

Compound	Tile drain no.	Depth of water, ^a cm	Residue ^b concn, $\mu\text{g/l}$.	Residue loss, g/ha
Atrazine	1	29.81 (April-December)	1.20	2.06
Deethylated atrazine	1		1.34	2.29
Deisopropylated atrazine	1		0.17	0.18
Cyprazine	2	21.85 (April-December)	0.64	1.21
Deethylated atrazine	2		0.65	1.22
Cyanazine	3	0.58 ^c (July)	0.50 ^c	0.02 ^c
Cyanazine amide	3	11.15 (April-December)	0.45	0.39
Deisopropylated atrazine	3		0.29	0.26
Metribuzin	4	0.71 ^c (July)	0.55 ^c	0.07 ^c

^a Calculated from daily flow data and expressed as centimeters per hectare of water. ^b These are average values calculated from the data given in Table III. ^c Cyanazine and metribuzin were detected only during the month of July at concentrations of greater than 0.01 $\mu\text{g/l}$. The losses were calculated by multiplying the total flow for July by the mean residue concentration.

tile-drain water were not observed after such a short period, in 1974. This is understandable in view of the much drier weather which prevailed for about 3 weeks following herbicide application. At the end of this period there was fairly heavy rainfall and a corresponding increase in the tile-drain flow rates. The results of the analyses suggest that the amount of rainfall may govern the quantity of herbicide residues in the tile-drain water. The precipitation values for the years 1971, 1972, 1973, and 1974 are 92.3, 119.1, 116.0, and 94.0 cm, respectively. The fact, however, that the water did not flow in the tile drain in mid-summer and that it was not feasible to collect samples after every rainstorm makes it impossible to draw definite conclusions as to effects of rainfall on the presence of herbicides in the tile-drain water.

From the results of the analysis of tile-drain water for herbicides and degradation products it was possible to estimate the loss of herbicide residues from the field via the tile-drain water. The estimates are shown in Table IV. Calculations showed that about 0.15% of the atrazine, cyprazine, cyanazine, and metribuzin that were applied appeared in the tile-drain water either in the unchanged form or as degradation products.

The triazine herbicide residue concentrations that were found in the tile-drain water are from 10 to 100 times lower than those that have been reported to affect marine algae (Hollister and Walsh, 1973). The impact of low levels of herbicide residues in drainage water on aquatic ecosystems needs further investigation.

Sirons et al. (1973) have shown that the concentration of deethylated atrazine is from 10 to 20% of that of the parent compound in the 0 to 2.5 in. depth of the soil following application. The detection of deethylated atrazine in the tile-drain water, at concentrations similar to or greater than those of atrazine, suggests that the deethylated compound, which is more polar than the parent compound, moves more rapidly through the soil. Likewise, cyanazine amide appears to move more readily than cyanazine.

It is hoped that the results of further studies will make possible the establishment of more or less precise relationships between the loss of herbicides from the soil via tile-drain water and such factors as soil type, texture, rainfall, and water solubility of the herbicides and degradation products.

ACKNOWLEDGMENT

The authors wish to thank Shell Research Ltd., Sittingbourne, England, for samples of cyanazine, cyanazine amide, and deethylated cyanazine, and Gulf Research Ltd. for samples of cyprazine and deethylated atrazine. We also appreciate the help and the continued interest of R. W. W. Evans (DuPont of Canada Ltd.).

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Received for review May 9, 1975. Accepted August 6, 1975. The authors appreciate the financial support of DuPont of Canada Ltd. and of the National Research Council, Canada for a scholarship held by one of us (D.C.M.).