Exposure Measurements of Applicators Spraying (2,4,5-Trichlorophenoxy)acetic Acid in the Forest

Terry L. Lavy,* J. Scott Shepard, and John D. Mattice

Personnel normally involved with spray applications in the forest were monitored for exposure to (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T). Seven members of a backpack crew, four from a tractor crew, and two 5-man helicopter crews assisted in this study. Crews followed usual spray routines with as little influence as possible from the test. External dermal and respiratory exposures were measured, and total intake of 2,4,5-T was determined from the total urine collected from each worker for a 6-day period. Analyses by gas chromatography showed that degree of exposure was related to worker's job. Greatest amounts were detected in mixers of the compound and least amounts in helicopter flagmen. Exposure to 2,4,5-T averaged 0.0005, 0.586, and 0.033 mg/kg body weight for inhalation, patch, and internal measurements, respectively. These measurements indicate that the worker excreting the highest amount of 2,4,5-T received exposure levels below those toxic to laboratory animals.

The herbicide (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T) has played an important role in the forest and food-producing capability of the United States during the past 20 years (Barrons, 1969). Its effectiveness in controlling a wide spectrum of broadleafed woody plants and its rapid degradation rate when applied to soil have allowed this herbicide to become widely used (Altom and Stritzke, 1973).

Research from animal feeding trials indicated that 2,4,5-T was fetotoxic and possibly teratogenic in mice when doses were administered in excess of 20 mg kg^{-1} day^{-1} (Roll, 1971). Fetotoxicity in rats was shown when 2,4,5-T levels of 25–150 mg kg^{-1} day^{-1} were used (Sparschu et al., 1971). On the basis of data such as these, on public reaction to stated effects of 2,4,5-T used in Viet Nam, and on localized public concern, the potential for 2,4,5-T to adversely affect human health has been questioned. The presence of trace levels of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), a highly toxic byproduct of the manufacturing process of the 2,4,5-trichlorophenol used to make 2,4,5-T, has also caused concern. Recent improvements in manufacturing technology have decreased the TCDD content in 2,4,5-T. Levels of TCDD in 2,4,5-T have dropped from 32 ppmw (late 1950's) to 2 ppmw (late 1960's) to 0.1 ppmw (early 1970's) (Young et al., 1978) to levels routinely below 0.01 ppmw (Fisher, 1977). Continuing concern over the implications of 2,4,5-T use in the United States was instrumental in its being placed on the list of compounds to be examined under a process initiated by the Environmental Protection Agency (EPA). This process, Rebuttable Presumption Against Registration (RPAR), was designed to allow a fair assessment of benefit–risk data before decisions regarding the future use of a compound are issued. The EPA RPAR Position Document 1 (*Federal Register*, 1978) pointed out a gap in the data on hand. The EPA had estimated that backpack sprayers receive approximately 7.0 mg/kg exposure, but actual amounts of 2,4,5-T received by 2,4,5-T applicators in forestry and other agricultural operations had not been directly measured. Our studies were designed to determine the levels of exposure occurring to field workers applying a low volatile ester formulation of 2,4,5-T during typical forestry applications.

MATERIALS AND METHODS

Field Operations. A single batch of ESTERON 245 herbicide (Lot MM-09447-76) was used for all of the studies. This product contains 4 lb of 2,4,5-T acid equivalent per gallon formulated as propylene glycol butyl ether ester. All workers included in crews of the following spray operations were monitored in these tests: backpack, tractor mist blower, and helicopter (both raindrop nozzle and microfoil boom). The low volatile ester was applied by backpack at a rate of 1.6 lb/A (acid equivalent basis) in 10 gal of water. Both the mist blower and helicopter operations used 2 lb/A in 10 and 5 gal of water per acre, respectively. Although ESTERON 245 is not labeled for mist blower application, permission was granted by the EPA to allow consistency in these studies.

Seven crew members, a mixer–supervisor, and six applicators made up the backpack team. Two of the applicators in this crew were females. The mist blower operation included a supervisor, two tractor drivers, and a mixer. Each of the two helicopter crews was made up of a pilot, a mixer, a supervisor, and two flagmen. Thus, a total of 21 workers, selected from a group who normally do this type of work in the area, were monitored in the study. Prior to this spray program, each worker filled out a form which provided personal information regarding his vital statistics and history of any previous involvements with 2,4,5-T use. Workers were selected who indicated that they had not worked with 2,4,5-T for 2 weeks prior to the study. Worker spray habits and routines, for the most part, did not include wearing gloves or special protective clothing. The typical attire for members of the spray crews included long trousers, shirt (long or short sleeves) and cloth sneakers, leather shoes, or field boots. Photographs of each worker and his spray attire were made immediately prior to the spray operation. All crew members wore hats except four members of the backpack crew.

In addition to the normal supervisory staff, additional support personnel were on hand to assist with data forms, attach monitors, record data, and transport samples collected. Research personnel involved with sample collection were instructed not to alter, make suggestions for, or interfere with normal spray habits or routines of the workers.

Potential Exposure Tests. To provide an estimate of 2,4,5-T ester exposure occurring via the respiratory tract, each worker wore a portable air pump which drew a known volume of air through a resin column (XAD-2) which trapped 2,4,5-T (Johnson et al., 1977). Approximately 6–7 L of air/h was monitored for 2,4,5-T as it was pulled through the resin. To serve as a control, two functioning air monitors were positioned in a nontreated field during

Department of Agronomy, Altheimer Laboratory, University of Arkansas, Fayetteville, Arkansas 72701.

0021-8561/80/1428-0626$01.00/0

the spray application period.

Estimates of the quantity of 2,4,5-T coming into contact with the bare skin portions of the body were made by attaching six cellulose backed gauze patches (10 × 10 cm) to each worker. Patches were modified versions of those described by Wolfe et al. (1975). The six patches were attached with safety pins to clothing on the chest, back, upper arms, and upper thighs. Only four patches were analyzed from each backpack crewman since the thigh patches were not durable enough to remain intact for the duration of the spray period. After the spray period, the patches were removed from each worker, placed together in an amber colored glass jar containing 400 mL of methanol, and transported to the laboratory for analysis. Total skin area exposed was calculated using photographs of each worker in his spray attire and technical information of the skin area of each body part given by Wolfe et al. (1975). For each worker, the total amount of 2,4,5-T detected per patch times the total skin area exposed equals the total dermal exposure.

Internal Exposure Tests. Since the total amount of 2,4,5-T in urine over a 5-day period has been shown to be a good indicator of the internal dose occurring to humans (Matsumura, 1970; Gehring et al., 1973), urine was collected and measured for 2,4,5-T content. The primary alteration of the 2,4,5-T ester as it enters the body appears to be its conversion to the acid form (Gehring et al., 1973). All 2,4,5-T values reported here are acid equivalents. The total urine excreted by each worker over a 6-day period for two exposure periods was collected in UR-24 Specimen storage containers, measured, and analyzed for 2,4,5-T content. Total urine excreted was collected from each 12-h period 1 day prior to spraying, on the spray day, and for at least 4 days following each spray operation. Since creatinine concentrations will remain nearly constant day to day in a given human body, these levels were also measured to determine whether the worker had provided a total, valid urine sample during each collection.

TCDD Analyses. In a nonreplicated study, the two gauze patches and one urine sample with highest concentrations of 2,4,5-T were analyzed to provide additional information regarding TCDD levels. Prohibitively demanding mass spectroscopy specifications did not permit replication in this phase of the study. The TCDD content was compared with the 0.040 ppm contained in the ESTERON 245 to determine whether 2,4,5-T degrades or is lost more readily than TCDD during the spray process.

Field Procedures. Each spray operation was conducted two times, separated by at least a 6-day interval. The majority of the spraying was completed in September, 1978, in the south central Arkansas region of the Southern Pine Belt where the terrain lies at a 0–10% slope. The actual spray dates, prevailing conditions, and duration of each spraying period are presented in Table I.

Workers were instructed to perform their routine duties in their usual manner with as little influence as possible from the test situation. A typical spray day proceeded as follows: The mixer would have prepared the spray mix the previous day; the crew assembled in the early morning hours (to take advantage of low wind and temperature conditions); project coordinators attached the air monitors and gauze patches to each crew member; the crew conducted the scheduled spray operation; and at the conclusion of the test, coordinators collected air monitors and gauze patches from the workers. Crew members were instructed not to purposely touch the patches. The project coordinators removed the patches from each worker at the end of the spray period and placed them compositely into an amber colored jar containing 400 mL of methanol. Workers kept their urine collection containers nearby but not directly in the spray area. All urine samples were transported to the laboratory and stored at 4 °C until analyses were completed.

Table I. Time and Weather Conditions for 2,4,5-T Spray Operations, South Central Arkansas Section of Southern Pine Belt, August to September, 1978

type applicator[a]	spray date	temp, °C	wind, mph	monitoring period,[b] min
backpack A	08/30	18–21	0–5	180
backpack B	09/06	18–24	0	173
tractor mist blower A	09/07	24–32	0	245
tractor mist blower B	09/21	19–34	0	200
aerial microfoil A	09/20	26	0	55
aerial microfoil B	09/26	18	2–5	117
aerial raindrop A	09/26	20	0–4	115
aerial raindrop B	10/03	20	0	116

[a] Letters A and B refer to the first and second spraying, respectively, in each of the tests conducted. [b] This time includes: fill-up time, spraying time, and one 10-min rest period for the backpack sprayers. Actual spraying time would be approximately 75–80% of the monitoring period.

Laboratory Analyses. Techniques of Mattice et al. (1979) were used in analyzing the patches and resin from the air samples. The gas chromatography allowed for quantitation of 0.15 μg of 2,4,5-T for the air samplers and 86 μg for the patches.

After the urine was delivered to the laboratory, a modification of a gas chromatographic technique by Nony et al. (1976) was used. Methylation was carried out directly in a benzene solution. Diazomethane was destroyed by the extraction with dilute HCl. Where further cleanup was needed, the technique described by Nony et al. (1976) was employed.

One urine and two patch samples were cleaned up and prepared for TCDD analysis following the general acid–base extraction procedure of Hummel (1977). The samples were made basic and extracted with hexane. The hexane was reduced in volume to ~5 mL and sent to the Midwest Center for Mass Spectrometry at the University of Nebraska–Lincoln, Department of Chemistry. There it was washed with H_2SO_4, neutralized, and passed through an alumina column before being separated with a 3% OV-3 on 100/120 Supelcoport gas chromatography column operated at a flow rate of 15 mL/min at 250 °C.

As TCDD eluted from the column, its mass was monitored at m/e 321.8936 which is the exact mass of $C_{12}H_4{}^{16}Cl_3{}^{37}Cl$ (native TCDD). The mass spectrometer was set for single ion monitoring using the standard peak switching of the MS-50. The source was operated at 250 °C and an ionizing energy of 70 eV.

RESULTS AND DISCUSSION

Potential Exposure by Dermal Absorption and Inhalation. Information derived from the dermal (patch) study shows that the backpack and mist blower workers received more 2,4,5-T exposure on their patches than did the helicopter crews (Table II). Workers 15, 16, 20, and 21, flagmen for the aerial spraying, received less exposure on their patches than most of the other 17 workers in the study (Table II).

Table II. Average Levels of 2,4,5-T Detected in Air (Resin), Skin (Patch), and Urine Samples per Exposure for Each Worker in Each Application Operation

spray operation and duty	worker no.	potential exposure: air (lung), μg/kg	potential exposure: skin, mg/kg	actual excretion: urine, mg/kg	correlation by crew, patch vs. urine
backpack					
supervisor/ mixer	1	nd	0.031	0.010	
sprayer	2	0.74	0.76	0.074	
sprayer	3	6.88	1.81	0.067	0.436
(F)[a]					
sprayer	4	nd	0.20	0.030	
sprayer (F)	5	0.36	0.82	0.023	
sprayer	6	0.48	2.54	0.038	
sprayer	7	0.68	1.47	0.052	
mist blower					
supervisor	8	0.11	0.20	0.029	
driver	9	0.30	1.58	0.034	
driver	10	0.24	0.99	0.036	0.603
mixer	11	0.19	1.62	0.078	
helicopter					
microfoil					
pilot	12	nd	0.11	0.005	
mixer	13	nd	0.12	0.065	
supervisor	14	nd	0.024	0.004	0.686
flagman	15	nd	nd	0.002	
flagman	16	nd	nd	0.001	
helicopter					
raindrop					
pilot	17	nd	nd	0.038	
mixer	18	nd	0.042	0.096	
supervisor	19	nd	nd	0.003	0.924
flagman	20	nd	nd	0.001	
flagman	21	1.03	nd	0.001	
				all workers	0.449

Female.

Detectable levels of 2,4,5-T were found in the air-monitoring devices for 10 of the 21 individuals monitored (Table II). Only one of the 10 helicopter crew members showed a detectable level. Potential inhalation exposure of the backpack crew was higher than that of the mist blower crew. No factual explanation for the higher 2,4,5-T air value reported for worker 3 (backpack sprayer) can be offered, but this resin probably became contaminated at some point in the study since the value is 10–15 times higher than most other values reported and the worker was performing the same tasks as other workers 2–7.

A comparison of the potential exposure via inhalation and skin absorption indicates that nearly 1000 times less 2,4,5-T could have been taken in through the lungs as through the skin. Evaluating exposure to worker 5, for example, the dermal study data (Table II) reveal a potential exposure of 0.82 mg/kg per spray period while the air exposure data show a potential exposure of 0.00036 mg/kg per spray period. In working very close to the spray, the backpack crew appeared to receive more exposure than other workers. However, the spray application mixture used by the backpack crew was less concentrated (1.6 lb/A 2,4,5-T in 10 gal of water) than the 2 lb/A in 5 gal of spray as applied in the other studies.

Potential Exposure and Excretion Levels. Inhalation exposure from 2,4,5-T was quite low compared to urine measurements (Table II). Correlation values between 2,4,5-T deposited on patches and that excreted in urine were also low for most of the comparisons made. For most workers, the maximum concentration of 2,4,5-T was excreted 1 day after spraying (Table III). By the end of day 2, all workers except 15 and 21, who both showed very low levels of 2,4,5-T in the urine, had excreted more than 50% of their total excretion measured. A relatively high correlation ($r = 0.81$) can be shown between the total 2,4,5-T excreted and the highest daily amount of 2,4,5-T excreted in the urine. This suggestion that a rather rapid and

Table III. Daily 2,4,5-T Excretion from Spray Workers for 6 Days Beginning 1 Day before Spray Operation

	exposure A, mg/kg × 10^{-3}						exposure B, mg/kg × 10^{-3}						
	days after spraying						days after spraying						
worker	background[a]	0[b]	1	2	3	4	background	0	1	2	3	4	total per exposure,[c] mg/kg × 10^{-3}
1[d]	1.6	2.5	2.9	1.7	2.1	1.2	1.0	0.5	2.3	1.7	2.3	2.6	9.90
2	5.9	8.6	21.4	21.5	10.6	6.2	10.6	11.5	30.4	13.4	14.4	9.7	73.85
3	0	9.5	22.1	33.0	12.4	4.4	5.4	4.9	22.9	4.7	9.9	11.0	67.40
4	1.5	2.7	10.3	4.4	5.2	2.9	3.6	8.0	4.2	11.6	6.1	5.3	30.35
5	0.6	2.4	14.8	4.8	4.2	1.9	2.7	1.9	3.6	7.0	2.5	2.3	22.70
6	5.7	8.7	15.6	7.0	3.6	3.2	2.8	2.6	0.2	*e*	*e*	*e*	38.10
7	11.4	2.8	31.1	11.4	11.7	10.2	7.6	4.3	12.0	9.5	4.9	5.6	51.75
8	0.9	7.3	9.0	6.1	4.0	2.7	*e*		2.9	2.1	1.5	1.4	29.10
9	1.2	4.1	17.6	8.2	6.9	4.4	1.2	7.7	8.5	2.7	5.7	1.1	33.45
10	6.5	6.7	7.0	7.3	7.1	4.7	8.9	7.9	10.0	5.1	8.4	8.4	36.30
11	0.5	15.7	28.6	20.8	8.2	5.1	*e*		20.6	15.2	3.6	3.5	78.40
12	0	0	0	0.4	0	0	0	2.4	3.3	2.8	1.0	0.9	5.40
13	17.4	22.3	12.9	16.8	12.7	10.4	12.5	13.5	12.8	12.3	8.9	6.8	64.70
14	0	0	0.3	1.3	1.8	0.4	0.1	1.2	0.7	0.4	0.1	1.0	3.60
15	0.3	0.1	0.6	0.3	0.2	1.5	0.1	0	0	0	1.0	0.1	1.90
16	0.4	0.1	0.4	1.4	0	0	0	0.3	0.5	0.2	0	0	1.45
17	4.0	6.4	8.3	11.7	5.6	5.0	4.5	5.1	11.2	8.3	8.3	6.3	38.10
18	8.3	8.7	25.9	10.2	10.6	9.3	11.1	12.9	41.0	25.9	28.2	19.1	95.90
19	0	0.2	1.9	1.2	0.9	0.8	0.6	0.2	0.7	0.4	0	0	3.15
20	0	0.8	0.9	0.7	0.2	0	0	0	0.3	0	0	0	1.45
21	0	0	0.3	0.3	0.3	0	0	0	0.2	0.2	0.1	0.8	1.10

[a] Background determination made 1 day before spraying. [b] Actual spray day. [c] Total per exposure was calculated using 2,4,5-T excreted in urine on the spray day and the 4 days following. [d] Worker 1, 11, 13, and 18 mixed the spray solutions on the day background samples were collected. [e] Sample lost in transit.

Table IV. Mean Exposures of 2,4,5-T Received as Determined by Urine Analysis: Classified by Spray Operation and Duty of Crew Member

spray operation	mean,[a] mg/kg	duty	mean, mg/kg
backpack	0.055 a	mixer	0.062 a
mist blower	0.044 a	backpack spray	0.047 a
aerial	0.022 a	mist blower driver	0.035 ab
		helicopter pilot	0.022 ab
		supervisor	0.011 b
		helicopter flagman	0.001 b

[a] Means within a group followed by the same letter are not different at the 0.05 significance level as determined by Duncan's multiple range test.

quantitative excretion of 2,4,5-T in the urine took place was confirmed by kinetic studies performed on these 2,4,5-T urine excretion data which showed that over 97% of the absorbed 2,4,5-T was excreted in urine within 7 days following exposure to the spray (Ramsey et al., 1979).

TCDD Analyses. The two patches containing the highest exposure of 2,4,5-T were analyzed for TCDD content. Sample A contained 20.59 mg of 2,4,5-T and 170 pg of TCDD. Sample B contained 30.53 mg of 2,4,5-T and 530 pg of TCDD. If the TCDD/2,4,5-T ratio on the patches remained constant from the time spray was prepared to the time the patch samples were analyzed, and if 100% was recovered, then 1220 pg of TCDD would have been detected in sample B. The technique may not have accomplished 100% recovery; however, recovery was at least 50%. Calculations based on a 50% recovery value show that the patch sample B contained 0.035 ppm TCDD at the conclusion of the study as compared to 0.040 ppm in the ESTERON concentrate initially used. No TCDD was detected in the urine sample containing the highest concentration of 2,4,5-T (3.12 mg/L). The analytical capabilities of the system could have detected as low as 140 pg of TCDD in this 85-mL sample.

Exposure and Work Duty. No significant difference in exposure level occurred between work crews. Data indicate that backpack and mist blower crews received more exposure; however, this exposure was not significantly different from that of the aerial crew (Table IV). Differences did, however, occur in relation to work duties within crews (Table IV). Totals per exposure ranged from a high of 0.096 mg/kg (mixer) to a low of 0.001 mg/kg (flagmen) for workers 18 and 21, respectively. Both were members of the helicopter raindrop crew. Except for worker 1, the mixer in each of the four crews showed higher exposure levels than any of his fellow crew members. These three mixers also had higher 2,4,5-T excretion values on day 0 than others in their crew probably because they mixed the 2,4,5-T the day before the actual spray occurred. Optimum preexposure data would have required the mixers to begin urine collection at least 1 day earlier. The fact that the fourth mixer (worker 1) endorsed cautious work habits and wore gloves may account for the comparatively low level of 2,4,5-T measured in his urine.

Categorized by work duties, mixers (those handling concentrate) received the highest internal exposure of 2,4,5-T, followed in order by backpack sprayers, mist blower drivers, helicopter pilots, supervisors, and flagmen for the helicopter operation. One helicopter pilot, worker 12, excreted considerably less 2,4,5-T in his urine than did the other pilot, worker 17 (Table III). Differences in pilot exposure appeared to be related to the fact that worker 17 routinely checked and unplugged nozzles at each fill-up time. In addition, he helped change the spray boom on the helicopter before and after each spray period.

Observations. Ninety-seven percent of any 2,4,5-T absorbed should be excreted within 7 days (Ramsey et al., 1979), and workers were instructed to avoid the compound for more than 7 days prior to the tests. However, several workers did show low levels of background exposure. Since adequate time had elapsed for complete excretion of 2,4,5-T, the workers with background levels probably had been exposed to the compound in some manner. Workers number 2, 6, and 7 had used 2,4,5-T more extensively than most of the other backpack crew members. Workers 10, 13, 17, and 18 also had had previous 2,4,5-T application experience. It is possible that work shoes or other clothing of some individuals contained 2,4,5-T when the study began. Workers may also have received these background exposures from containers, spray equipment, or vehicles contaminated with the compound. In the effort to alter the workers' routines as little as possible, no effort was made to isolate these individuals from all sources of contamination before the spray operations began.

Field observations suggest that exposure could be reduced if work habits were altered. Protective clothing that was free from contamination, including footwear, long sleeves, and gloves probably could have decreased exposure. For example, in handling the concentrate, the mixers had a greater chance of skin exposure through the hands than did other workers. As indicated earlier, worker 1, who wore gloves while performing the same mixing duties as workers 11, 13, and 18, excreted significantly lower levels of 2,4,5-T in his urine than did the other three workers who did not wear gloves (Table III).

In these studies, conducted without alterations in the habits and spray routines of field workers, none of the data revealed levels of 2,4,5-T that would appear to constitute a hazard to health. The amounts excreted were well below the toxicity levels observed in laboratory tests with mice and rats (Roll, 1971; Sparschu et al., 1971). The greatest individual exposure was considerably less than the 7.0 mg/kg for backpack sprayers which the EPA working group (*Federal Register*, 1978) had predicted for this type of spray operation.

ACKNOWLEDGMENT

The authors appreciate the support of the National Forest Products Association in conducting this study and Martha Davis for her assistance in manuscript preparation.

LITERATURE CITED

Altom, J. D., Stritzke, J. F., *Weed Sci.* **21**, 556 (1973).
Barrons, K. C., *Science* **165**, 465 (1969).
Federal Register **43** (78); 17116–17157 (April 21, 1978).
Fisher, J. R., Letter p. G-12 in Final EIS, Vol. 1, USDA Forest Service, 1977.
Gehring, P. J., Kramer, C. G., Schwetz, B. A., Rose, J. Q., Rowe, V. K., *Toxicol. Appl. Pharmacol.* **26**, 352 (1973).
Hummel, R. A., *J. Agric. Food Chem.* **25**(5), 1049 (1977).
Johnson, E. R., Yu, T. C., Montgomery, M. L., *Bull. Environ. Contam. Toxicol.* **17**(3), 369 (1977).
Matsumura, A., *Sangyo Igaku* **12**, 446 (1970).
Mattice, J. D., Lavy, T. L., Lea, R. E., unpublished data, Altheimer Laboratory, University of Arkansas, Fayetteville, 1979.
Nony, C. R., Bowman, M. C., Holder, C. L., Young, J. F., Oller, W. L., *J. Pharm. Sci.* **65**(12), 1810 (1976).
Ramsey, J. C., Lavy, T. L., Barun, W. H., unpublished data, Altheimer Laboratory, University of Arkansas, Fayetteville, 1979.
Roll, R., *Food Cosmet. Toxicol.* **9**, 671 (1971).
Sparschu, G. L., Dunn, F. L., Lisowe, R. W., Rowe, V. K., *Food Cosmet. Toxicol.* **9**, 527 (1971).

Wolfe, H. R., Armstrong, J. F., Staiff, D. C., Comer, S. W., Durham, W. F., *Arch. Environ. Contam. Toxicol.* **3**, 257 (1975).
Young, A. L. Calcagni, J. A., Thalken, C. E., Tremblay, J. W., Technical Report OEHL-TR-78-92 USAF Occupational and Environmental Health Laboratory, Brooks Air Force Base, TX, 1978.

Received for review August 13, 1979. Accepted January 14, 1980. Published with the approval of the Director of the Arkansas Agricultural Experiment Station.

Use of Ethylation for the Gas and Liquid Chromatographic Determination of Linuron, Diuron, and Metoxuron and Two of Its Degradation Products: Application to Soil Analysis

James F. Lawrence,* Carmen Van Buuren, Udo A. Th. Brinkman, and Roland W. Frei

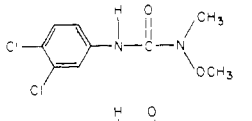
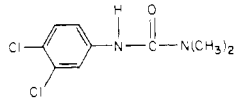
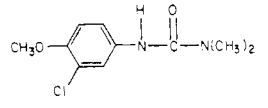
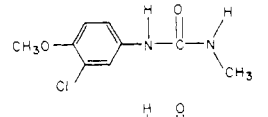
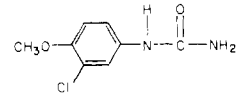
The urea herbicides linuron, diuron, and metoxuron and its metabolites, monomethylmetoxuron and desmethylmetoxuron, were ethylated using ethyl iodide and sodium hydride in dimethyl sulfoxide, with a reaction time of 30 min at room temperature. The products proved to be exceptionally stable and well suited to gas chromatography. The structures were confirmed by gas chromatography–mass spectrometry. Separation of all the test compounds as their ethyl derivatives was achieved by both gas and liquid chromatography. Successful determination of metoxuron and diuron in soil at 1.0 ppm was accomplished by both gas and liquid chromatography. Selective nitrogen–phosphorus detection proved to be superior to electron-capture determination of the two herbicides in soil. Direct liquid chromatographic determination of the two ureas in soil was also possible. The minimum detectable concentrations of metoxuron in the samples was estimated to be less than 50 ppb by gas chromatography with nitrogen–phosphorus detection. The reproducibility of replicate standards carried through the ethylation procedure and analyzed by gas chromatography was 6% relative standard deviation.

The direct gas chromatographic (GC) analysis of many urea herbicides has been reported (Buser and Grolimund, 1974; Katz and Strusz, 1969; McKone, 1969; McKone and Hance, 1968; Spengler and Hamroll, 1970). However, a significant number of these compounds are thermally unstable, decomposing partly to isocyanates and amines (Buchert and Lokke, 1977; Saunders and Vanatta, 1974). The main contributing factor in the decomposition is the N–H moiety of the molecules. Attempts at blocking this group by alkylation (Buchert and Lokke, 1977; Saunders and Vanatta, 1974; Lawrence and Laver, 1975; Tanaka and Wien, 1973), acylation (Saunders and Vanatta, 1974; Ryan and Lawrence, 1977), and silylation (Fishbein and Zielinski, 1965) have been reported. Of these reactions, the alkylated products are the most stable derivatives in the presence of water. The silyl and acyl products tend to hydrolyze back to the original ureas.

Methyl iodide in the presence of sodium hydride has been used successfully for alkylating several urea herbicides for GC determination in a number of foods (Lawrence and Laver, 1975). However, such a derivatization technique cannot distinguish between the N-demethylated degradation products of ureas such as linuron or metoxuron. On the other hand, ethyl iodide as the alkylating agent eliminates this problem and has been successfully applied to the chromatography of some degradation products of linuron (Glad et al., 1978).

In the present study this same alkylation technique with ethyl iodide has been investigated for application to the GC separation metoxuron, monomethylmetoxuron (MMM), desmethylmetoxuron (DMM), linuron, and diuron. The suitability of this technique for analysis of soil spiked with metoxuron and diuron is demonstrated. A comparison is made between this method and direct liquid chromatography (LC) of the ureas (Lawrence, 1976) in terms of sensitivity and suitability for residue analysis.

Table I. Structures of the Ureas

name	chemical structure
linuron	
diuron	
metoxuron	
monomethylmetoxuron (MMM)	
desmethylmetoxuron (DMM)	

EXPERIMENTAL SECTION

Reagents. The chemical structures of the ureas studied are shown in Table I. All were obtained from Sandoz Ltd. (Basel, Switzerland). Sodium hydride was obtained from J. T. Baker (Deventner, The Netherlands) as a 50% oil dispersion. About 2 g of the material was washed with hexane and then stored in a small, tightly sealed, screw-capped vial when not in use. The soil sample was obtained

Food Research Division, Food Directorate, Health Protection Branch, Tunney's Pasture, Ottawa, Ontario K1A 0L2, Canada (J.F.L.), and the Analytical Chemistry Department, Free University of Amsterdam, 1083 De Boelelaan 1081 HV, Amsterdam, The Netherlands (C.V.B., U.A.T.B., R.W.F.).

0021-8561/80/1428-0630$01.00/0