Persistence, Leachability, and Lateral Movement of Triclopyr (Garlon) in Selected Canadian Forestry Soils

Gerald R. Stephenson,*,† Keith R. Solomon,‡ Cindy S. Bowhey,† and Karsten Liber†

Department of Environmental Biology, University of Guelph, Guelph, Ontario N1G 2W1, Canada, and Canadian Centre for Toxicology, 645 Gordon Street, Guelph, Ontario N1G 1Y3, Canada

Triclopyr [[(3,5,6-trichloro-2-pyridyl)oxy]acetic acid, Garlon 4E] was moderately persistent in sandy and clay soils at a Northern Ontario site. Times to 50% and 90% disappearance were 2 and 4 weeks, respectively, regardless of soil type. Evidence of triclopyr leaching in response to heavy rainfall was observed 7 days after application in both soils, but residues of triclopyr at a depth of 25–30 cm never exceeded 6 μg/kg, when present. In a study of lateral movement of triclopyr with runoff water, residues (in the range 0.01–0.96 μg/L) were recovered in a collection ditch 12–13 m downslope; however, there was no evidence of mass movement of triclopyr at quantifiable levels (0.54 μg/kg) downslope in the soil. Field studies of persistence and mobility confirmed earlier laboratory results and indicate that environmental problems are unlikely to occur as a result of excessive triclopyr persistence and/or mobility in soils typical of Northern Ontario forestry areas.

Triclopyr [[(3,5,6-trichloro-2-pyridyl)oxy]acetic acid, Garlon 4E], a pyridine herbicide, is highly active for the control of broad-leaved weeds and brush but has little activity on grasses (Byrd et al., 1974). Like its two close analogues, 2,4,5-T and picloram, triclopyr induces characteristic auxin-type responses in affected broad-leaved plants (Radosevich and Bayer, 1979). Although triclopyr has been used for several years to control brush in rangelands of the United States (Bovey and Mayeux, 1980), it is just now being considered for use on rights-of-way and for conifer release in Canada.

In a study conducted in a Northern Ontario Lake, triclopyr was found to be no more persistent in water than 2,4-D (Solomon et al., 1988). Only 5% of the chemical was present after 15 days, and detectable residues were not observed beyond 42 days. On the other hand, dissipation of triclopyr in soil has not been examined extensively.

In laboratory studies of triclopyr leachability in soil columns, Lee et al. (1985) found that all residues remained in the top 10 cm of the column. After 54 days of simulated precipitation (2.5 cm every second day), total recovered residues accounted for 65% of applied and, of this, 85% was in the form of the 3,5,6-trichloro-2-pyridinol metabolite. Norris et al. (1987) examined the dissipation of triclopyr in two pasture situations in Oregon. They estimated the half-life of triclopyr in soil to be approximately 80 days. Very low levels of the pyridinol and pyridine metabolites were detected, but they were not persistent. Only traces of triclopyr or its metabolites were recovered at depths greater than 30 cm in soil. Jotcham et al. (1989) compared the persistence of triclopyr, picloram, and 2,4,5-T under field conditions in a Southern Ontario agricultural soil. Triclopyr was found to be slightly less persistent than 2,4,5-T, but both herbicides were much less persistent than picloram. Two months after application of 3.84 kg/ha to a sandy-loam soil, triclopyr was no longer toxic to lentils as a bioassay plant. Jotcham et al. (1989) also compared the mobility of the acids of [^{14}C]triclopyr, [^{14}C]-2,4-D, and [^{14}C]picloram by means of soil thin-layer chromatography. Regardless of soil type, triclopyr was significantly less mobile than picloram but very similar in mobility to 2,4-D.

The objectives of this study were to examine the persistence, leachability, and lateral movement of triclopyr under field conditions in two Northern Ontario forestry soils.

Table I. Characteristics of the Study Soils

property	soil fraction[a]	clay site vertical leaching	clay site lateral movement	sand site vertical leaching	sand site lateral movement
pH	OL	5.0	5.4	4.5	4.1
	ML	5.4	4.9	5.0	4.8
% clay	OL				
	ML	53.4	60.3	5.0	3.3
% silt	OL				
	ML	39.0	33.2	7.9	15.1
% sand	OL				
	ML	7.4	6.5	87.1	81.7
% organic matter	OL	74.2	24.6	33.8	12.9
	ML	3.4	2.2	5.2	1.6
CEC, mequiv/100 g	OL	69.5	69.5	15.5	
	ML	179.2	13.7	3.1	1.8

[a] Key: OL, organic layer; ML, mineral layer to a depth of 30 cm.

MATERIALS AND METHODS

Selection of Field Sites. A number of possible sites were investigated in the Matheson area of Northern Ontario. The first objective was to find level locations on the sand and clay soils typical of this forestry area that were suitable for a persistence study. The second objective was to find nearby sloping areas that would permit studies on lateral movement on similar soils. The sand site was located 30 km east of Matheson in Harker Township (79°48′ W:48°30′ N) and had been planted with jack pine (*Pinus banksiana* Lamb) 4–5 years previously. The soil was an orthic-ferric podzol (Table I). The clay site was located 30 km away in Lamplugh Township (79°47′ W: 48°38′ N) and was a cut-over grassy area with scattered mature deciduous trees. The soil was an orthic-humic gleysol (Table I).

Persistence and Vertical Movement Study. A 20 × 20 m experimental plot was staked out at each of the sand and clay sites. All dead wood, live brush, and as much of the low vegetation as possible were removed from the plots by hand-clearing. The spray plots were divided off with pegs and twine. Each of five replicate spray plots consisted of a 2-m-wide strip, 20-m

† University of Guelph.
‡ Canadian Centre for Toxicology.

0021-8561/90/1438-0584$02.50/0

Table II. Calculated and Actual Rates of Application

replicate	application rate, kg/ha		
	calcd	Petri dish[a]	soil
Sand Vertical Persistence			
A	4.05	3.58	3.80
B	3.45	2.82	0.74
C	3.15	2.54	1.73
D	2.75	2.68	4.93
E	3.00	2.44	1.98
mean	3.28	2.81	2.64
SE	0.20	0.18	0.68
Sand Lateral Movement			
strip	2.7	2.86	
Clay Vertical Persistence			
A	2.85	3.61	4.63
B	2.9	3.89	2.61
C	3.12	4.09	2.51
D	2.88	4.46	3.53
E[b]	2.5	6.45	7.61
mean	2.85	4.50	4.18
SE	0.09	0.45	0.84
mean without replicate E[b]	2.94	4.01	3.32
Clay Lateral Movement			
strip	3.0	3.31	

[a] Mean of three replicates per treated strip. [b] In replicate E at the clay site, one of the nozzles became plugged during treatment. This resulted in a lower total volume applied and a higher application rate on one side of the plot. Since the Petri dishes were placed in the sprayed half of the plot, soil sampling was carried out in the sprayed half as well. Initial residues may have been artificially high for this reason.

length, and were separated by an unsprayed buffer strip 1–2 m wide. These treatment plots were subdivided into 10 subplots each 2 m × 2 m for sampling purposes.

Lateral Movement Study. Both the sand (slope 8°) and clay (slope 7°) plots were cleared of all dead wood and other matter that may have caused channeling of surface waters. A strip of soil at the top of each slope was cleared as above for spraying. The plots were marked with wooden posts and divided into sampling zones. A back hoe was used to dig a water-collecting trench (25 m long × 1 m wide × 0.5 m deep) at the bottom of each slope. The trench was lined with 6-mil black polyethylene sheeting to prevent water from draining out, and the upslope edge of the plastic was anchored into the side of the trench in such a way as to ensure that runoff water from the site was directed into the trench. The trenches were located 12 and 13 m downslope from the sprayed strip at the sand and clay sites, respectively.

Soil surface temperature was recorded with a maximum–minimum thermometer at each site. Rainfall was recorded continuously at both sites by means of a tipping-bucket rain gauge. This instrument facilitated an estimate of total rainfall between sampling periods, but this total could not be separated into rainfall events on particular dates. Information on rainfall during each 24-h period was available from a weather station at nearby Matheson.

Treatment. On June 18 the sites were treated with triclopyr as Garlon 4E butoxyethanol ester formulation (480 g/L AE). A Pestex backpack sprayer (Thompson et al., 1984) with a 2-m boom and four evenly spaced Tee-Jet AL 8004 nozzles was operated at a pressure of 200 kPa at a boom height of 0.3–0.5 m. The intended rate of application was 3 kg/ha: Actual amounts of spray applied per strip are summarized in Table II. As an additional check of the application rate, three 10-cm glass Petri dishes were placed in each strip. Immediately after the strip was sprayed, deposits in the dishes were collected with three successive 50-mL rinses of acetone that were combined and stored at −17 °C until analysis. The site at which the plate was positioned was marked so as to prevent its use as a site for soil sampling.

Sampling. Randomly assigned subplots within the plots were sampled at predetermined times. Samples were taken with a

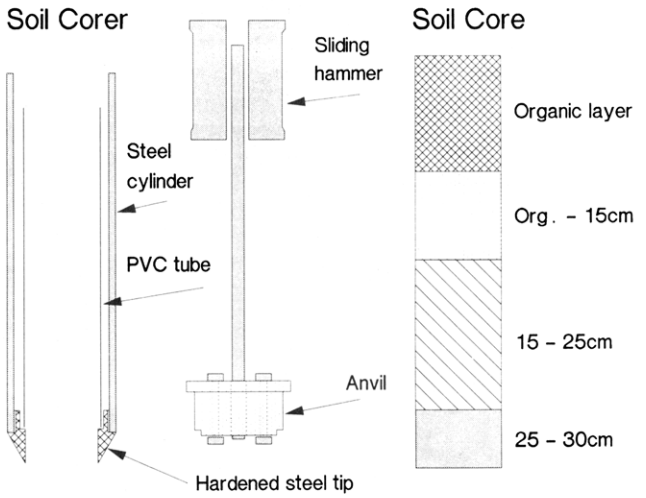

Figure 1. Construction details of the soil corer and the division of the soil cores.

75-mm-diameter soil corer (Figure 1), placed to avoid surface obstacles. A new PVC liner tube was inserted into the corer for each sample, and the corer was driven 30 cm into the soil with the aid of the sliding hammer. The surrounding soil was carefully shoveled away from the corer and the corer tipped over to an angle of 45° to facilitate removal. The PVC liner tube containing the core was removed with needle-nosed pliers, the open ends were sealed with aluminum foil held in place with tape, and the sample was placed in a new polyethylene bag. Before further use, the cutting edge and anvil of the corer were wiped clean. In this way, cross-contamination between samples was reduced to a minimum. The cores were transported to a freezer within 24 h of collection and were stored at −17 °C until transport to the laboratory for analysis. Residue analyses of samples stored for up to 6 months under these conditions showed losses of <5%. In preparation for analysis, the PVC tube was cut end to end on two sides with a table saw (without cutting into the soil), opened, and allowed to thaw slightly. Each soil core was then divided into four sections: organic layer, organic layer to 15 cm, 15–25 cm, and 25–30 cm (Figure 1).

For the lateral study, sampling began at the lower outside edge of the plot and moved upward and inward to avoid contamination from high- to low-concentration areas. In these cores the soil was removed from the PVC core tubes and bagged as the protocol did not require sectional analysis of the core. Samples were stored as above. Composite 1-L water samples were taken from each trench in clean glass bottles.

Analysis. Residues of triclopyr were concentrated from water samples in the field with XAD-2 and XAD-7 resins and eluted with diethyl ether (Solomon et al., 1988). Ether extracts of the water samples were transferred to methanol, hydrolyzed, then methylated with BF_3, and analyzed by gas–liquid chromatography (Solomon et al., 1988).

Soil core sections were broken up by hand and all stones and small sticks removed. The soil was mixed thoroughly and the total mass recorded. Subsamples of sand and clay (100 and 200 g, respectively) were placed in a 1-L glass jar with 400 mL of acetone/hexane (1:1) acidified with 6 mL of 37 N H_2SO_4. To facilitate suspension and extraction of the clay samples, the extraction mixture was first homogenized with 200 g of anhydrous granular sodium sulfate. All samples were agitated on a shaker for 1 h. After the soil fraction was allowed to settle, the solvent was decanted through glass fiber filter paper into a 1000-mL boiling flask. The remaining soil/solvent mixture was centrifuged at 750g for 12 min, and the supernatant was filtered and added to the appropriate boiling flasks. The clay extracts were reduced to a volume of approximately 50 mL on a rotary evaporator and were transferred to a large separatory funnel containing 100 mL of 0.01 N NaOH. This alkaline aqueous extract was washed by liquid–liquid partitioning with 3 × 25 mL volumes of hexane, and the hexane fractions were discarded. The aqueous fractions were then acidified to pH <2.0

Table III. Recovery Efficiencies for Triclopyr Acid (A) and Butoxyethanol Ester (B)

matrix	herbicide	concn	mean recovery, %	LOD[a]	LOQ[a] (±SE)
water	A	100 μg/L	66.3 (4.1)	0.005	0.01 μg/L
	B		87.5 (1.6)	0.005	0.01 μg/L
organic matter	A	4 mg/kg	71.9 (2.7)	0.27	0.54 μg/kg
	B		73.9 (4.2)	0.27	0.54 μg/kg
clay	A	500 μg/kg	86.7 (4.0)	0.27	0.54 μg/kg
	B		69.4 (3.4)	0.27	0.54 μg/kg
sand	A	1 mg/kg	85.4 (3.7)	0.27	0.54 μg/kg
	B		65.5 (4.8)	0.27	0.54 μg/kg

[a] Key: LOD, limit of detection; LOQ, limit of quantitation.

with 37 N H_2SO_4, and a second liquid-liquid partition was performed, this time with three volumes (50, 25, 25 mL) of ethyl acetate. The ethyl acetate fractions were combined and filtered through anhydrous Na_2SO_4 into a 500-mL glass boiling flask.

The decanted sand extracts in the boiling flasks were evaporated down to 50 mL and were transferred to a 500-mL separatory funnel containing 100 mL of 3% NaCl acidified (pH <2) distilled water. A liquid–liquid partition was performed with three volumes (50, 25, 25 mL of diethyl ether). These ether extracts were also combined and filtered through anhydrous Na_2SO_4 into a 500-mL boiling flask.

All extracts were rotary-evaporated down to 2–5-mL volumes and transferred to a 20-mL glass test tube with methanol. These were evaporated down to 5-mL volume under a flow of nitrogen. A 1.0-mL volume of 0.1 N NaOH was added to each extract. The tubes were tightly capped and placed in a water bath at 65 °C for 30 min. After cooling, 1.5 mL of 0.1 N H_2SO_4 and 1.0 mL of BF_3 (14% BF_3 in methanol) were added and the resultant mixture was held in a water bath for 45 min at 90 °C. After cooling, each sample extract was transferred to a 60-mL separatory funnel containing 25 mL of distilled water. A liquid–liquid partition into pertroleum ether was then performed (3 × 5 mL). The ether fractions were combined and were filtered through anhydrous Na_2SO_4 into test tubes. Isooctane (1 mL) was added to each ether extract (as a keeper) prior to evaporating the mixture down to a volume of 1.0 mL in a stream of dry nitrogen.

Samples were cleaned by column chromatography. A deactivated (4% water) acidic alumina column was prepared with use of 10 g of acidic alumina overlayed with 2 g of Na_2SO_4. The 1-mL isooctane extract (above) was transferred to the column, and the column was eluted with 25% diethyl ether in hexane. The fraction from 8 to 28 mL was collected. One milliliter of isooctane was added, the ether/hexane removed by evaporation, and the volume brought to 10 mL with isooctane.

The samples were analyzed by gas–liquid chromatography (2000 × 3 mm column packed with 3% OV 17 on 80/100 Gas-Chrom Q, using an electron capture detector) as previously described (Solomon et al., 1988).

RESULTS AND DISCUSSION

Recovery efficiencies from spiked, field-collected samples are shown in Table III.

There were only slight differences in the temperatures recorded at the sand and clay sites. The average on-site day temperatures were similar to the long-term average temperatures recorded at Timmins, Ontario, for the years 1951–1980 (Figure 2). Thus, with respect to June through September temperatures, our study sites were quite normal for the area.

Rainfall data at the two sites were in agreement with those of Matheson (Figure 3). The long-term average rainfall recorded at Timmins, Ontario, is 90 ± 44 mm for June and 98 ± 58 mm for July (Environment Canada, 1981). Thus, rainfall was above the normal range for June and within the normal range for July. Furthermore, there was rainfall between all sampling times.

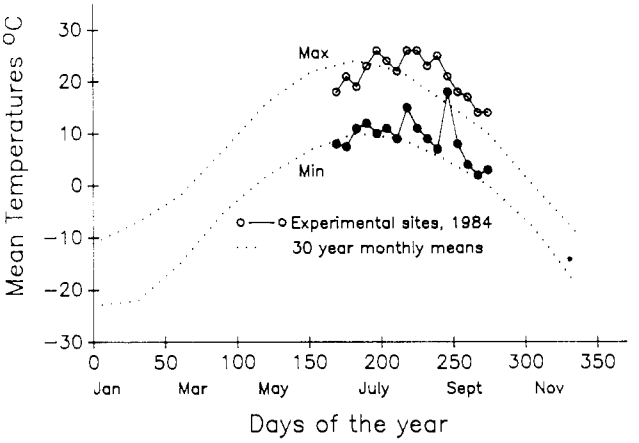

Figure 2. Maximum and minimum temperatures at the field sites and 30-year monthly means of Timmins, Ontario.

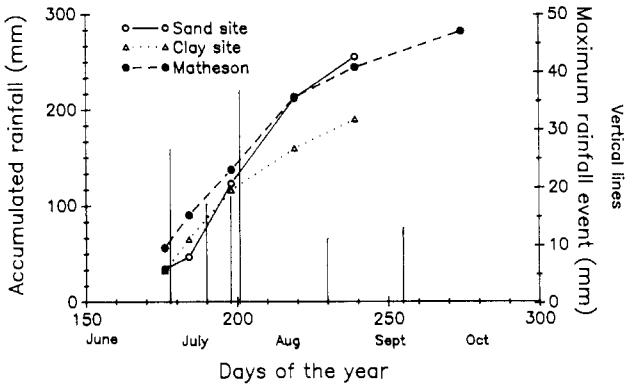

Figure 3. Accumulated rainfall at the sand site, clay site, and Matheson, Ontario, during the sampling period and weekly maximum rainfall events at Matheson.

Initial Recoveries. The intended application rate for triclopyr was 3.0 kg/ha. Based on actual spray volumes applied, the average rates of application were estimated to be 3.28 and 2.85 kg/ha at the sand and clay sites, respectively (Table II). However, analysis of the Petri dish collectors gave a better estimate of the initial soil application rate (Table II). Due to a plugging of one nozzle in replicate E at the clay site, only one side of the strip was treated uniformly. The Petri dishes were on this side, and soil sampling was confined to this side as well. It is apparent from these data that the treated side of this strip received a higher rate of triclopyr (Table II). The data for replicate E were included in the calculation of dissipation as it was felt that the rate of application, although higher than normal, was within the range of variation that might be expected under actual use conditions. The spray zones in both the sand and clay lateral movement areas received 2.7 and 3.0 kg/ha, respectively. These were close to the values estimated with Petri plate residues: 2.86 and 3.31 kg/ha (Table II).

Persistence. Data on triclopyr persistence or lateral movement in soil are expressed as total micrograms per soil core or per soil sampling depth. Since the area of the soil core was 45.6 cm^2, 1 μg/core would be equivalent to 2.19×10^{-3} kg/ha. Initial dissipation of triclopyr was rapid in both soil types investigated. The time required for 50% dissipation was approximately 2 weeks regardless of soil type. By 4 weeks after treatment, recoverable residues had decreased to less than 10% of those recovered at 0 time. However, from that point on, further dissipation was not apparent. From 4 to 48 weeks after treatment, recoverable residues remained at approx-

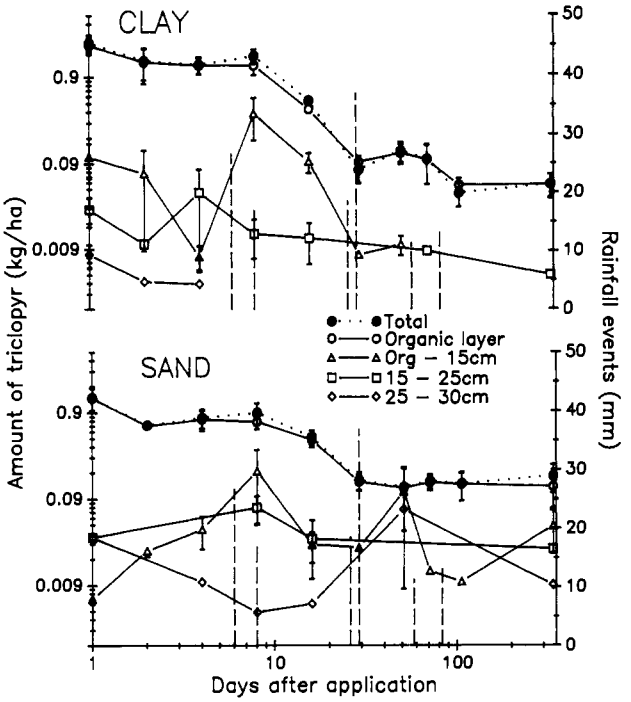

Figure 4. Dissipation of triclopyr at different depths at the clay and sand sites. Each point is the mean of five replicate samples; standard errors are indicated by the vertical bars, and the vertical dashed lines show the weekly maximum rainfall events. Both x and y axes are logarithmic scales. The residue concentrations in the organic layer and the total core are so close that the points overlap for a number of the sampling periods.

imately 10% and 4% (114 or 70 μg/core) at the sandy site or clay site, respectively. On a weight/weight basis, these residues would be approximately 55 μg/kg at the sand site and 35 μg/kg at the clay site. Such levels would not be expected to injure highly sensitive broad-leaved plant species (Jotcham et al., 1989).

Total residues in the cores (Figure 4) were subjected to statistical analysis by means of linear regression and analysis of covariance of the transformed data. The lines of best fit were as follows:

$$\text{sand:} \quad \log Y = 3.02 - 0.444 \log X \qquad r^2 = 0.783$$

$$\text{clay:} \quad \log Y = 3.37 - 0.770 \log X \qquad r^2 = 0.856$$

Analysis of covariance indicated that the slopes of the lines were significantly different ($p < 0.05$). Rate of dissipation in clay was significantly more rapid than in sand soil. It sould be noted, however, that this phenomenon is probably associated more with differences between the organic matter layers in the two soils than the mineral layers. Almost all residues recovered were in the organic layer (Figure 4), and as these had different properties (Table I), this may explain the difference in rates of dissipation.

Vertical Movement. In a study of pesticide movement, rainfall during the first several days after application is probably the most significant. During the first week (days 0–7), 33 and 34 mm of rain were recorded at the clay site and sand site, respectively (Figure 3). The largest rainfall event during this period occurred on the sixth day just prior to our fourth sampling. Most herbicide applications for conifer release in this area are made in late August, and rainfall is normally lower at that time than in June. Thus, if anything, this study represents a worst case study.

At all sampling times, 90% or more of the triclopyr was recovered from the upper organic layer at both locations and 97% or more was recovered within the top 15 cm of the soil core (Figure 4). The most significant evidence of leaching was observed on day 7 (Figure 4) possibly in response to the rainfall event on day 6.

The clay site was heavily covered with herbaceous vegetation, and the surface organic layer was thick (5–10 cm). In comparison, the vegetative cover at the sand site was sparse and the organic layer was much thinner (0.5–4 cm). Despite these obvious differences, there was very little, if any, difference in the leachability of triclopyr at the two sites. These results are similar to those obtained by Norris et al. (1987) in pasture soils.

Finally, there was some evidence that the sampling procedure itself (i.e., pounding the soil corer through moist soil) could be responsible for carrying some triclopyr residues to lower soil zones. This was particularly evident at 0 time in the clay soil where more than 100 μg of triclopyr was carried below the organic layer even though there was no time for leaching. A light misty rain that occurred at sampling time at the clay site but not at the sand site could have been a contributing factor. It is possible that the leaching observed after day 7 was the result of contamination of lower layers of soil during coring in the rain-soaked soils; however, there are insufficient field or laboratory data to substantiate this hypothesis.

Lateral Movement. Residues of triclopyr in the quantifiable range (0.54 μg/kg) were never detected in soil downslope from the sprayed strip in either the sandy soil or clay soil. At the limit of quantitation (about 1 μg/core), the residue present in soil would be equivalent to 2.4 g/ha. This is 3 orders of magnitude less than the application rate and is also well below the threshold for biological activity (Jotcham et al., 1989). Residues in soil as a result of lateral movement are therefore unlikely to be of biological significance.

Because of a 200–300-fold greater sensitivity for detecting triclopyr in water, analyzing runoff water was a more appropriate parameter for measuring lateral movement of triclopyr than soil analysis. Analysis of the water collected in the trenches revealed that low concentrations of triclopyr (<1 μg/L) were present in runoff water from 1 to 105 days after treatment. These residues are unlikely to be of biological significance. The source of these early residues may have been drift or some runoff from rain on the day of treatment. Triclopyr has been shown to dissipate rapidly from water (Solomon et al., 1988), and residues in water resulting from spray drift would not be expected to persist to the extent suggested by these results. These observations therefore suggest that some runoff or erosion of soil occurred at later times during the study and carried triclopyr into the trench.

Although the detection limit for triclopyr in water was much lower than for soil, the method used to collect runoff water in this study had several disadvantages. We were unable to measure actual runoff volume, and we lacked a mechanism to separate runoff from different rainfall events. Such sophistication was beyond the resources of this study but would have allowed more useful measurements to be made.

The minimal leaching of triclopyr in response to heavy rainfall and the lack of observation of biologically significant lateral movement of triclopyr with runoff water confirmed earlier laboratory results. These results suggest that environmental problems are unlikely to occur as a result of excessive triclopyr presistence and/or mobility in soils typical of Northern Ontario forestry areas.

ACKNOWLEDGMENT

This work was supported by the Canadian Forestry Service Program of Research by Universities and the Ontario Ministry of Agriculture and Food. We thank Bob Dennis, Ken Maynard, and Dr. R. Campbell of the Ontario Ministry of Natural Resources and Drs. P. Reynolds, P. Kingsbury, and R. Prasad of Forest Pest Management Institute for their help, advice, and assistance.

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Received for review April 10, 1989. Accepted September 12, 1989.

Registry No. Triclopyr, 55335-06-3.

Recovery of Protein-Rich Byproducts from Oat Stillage after Alcohol Distillation

Y. Victor Wu

Northern Regional Research Center, U.S. Department of Agriculture—Agricultural Research Service, 1815 North University Street, Peoria, Illinois 61604

Ground oats, ground groats, and oat flour were fermented to ethanol. After ethanol was distilled, residual stillage was separated by screening and centrifugation into distillers' grains, centrifuged solids, and stillage solubles. Oat distillers' grains and centrifuged solids had crude protein contents (nitrogen × 5.83, dry basis) of 19 and 44%, respectively, and contained 67 and 5% of the total nitrogen of oats. Oat flour distillers' grains and centrifuged solids had 43 and 48% protein, respectively, and accounted for 13 and 58% of the total nitrogen of oat flour. Of the nitrogen in oat stillage solubles, 54% passed through a 10K molecular weight cut-off membrane. Permeate from oat stillage solubles processed by combined ultrafiltration and reverse osmosis had much lower nitrogen, solids, and ash contents than did stillage solubles. This practical method to ferment ground oats and oat flour for ethanol and to recover valuable protein-rich byproducts may have commercial potential.

Corn is the most common biomass for commercial ethanol production in the United States (Morris, 1983). After ethanol is distilled, a protein-rich residue (stillage) that contains 5–10% solids remains. This stillage is screened or centrifuged to yield an insoluble solid, corn distillers' dried grains. The remaining soluble fraction with 2–4% solids content is usually evaporated to a syrup and dried with the solids from screening or centrifugation. Drying the soluble fraction requires considerable energy, but discarding this fraction would result in serious pollution.

Ultrafiltration is an efficient process for selectively separating solutions by convective solvent flow through a membrane at moderate pressure. Solutes or particles larger than the specified membrane "cut-off" are quantitatively retained, but solutes smaller than the membrane pores pass through with the solvent. Reverse osmosis separates water from a solution by a membrane that is more permeable to water than to ions and other dissolved matter (Gregor and Gregor, 1978). The solution is pumped at high pressure across the membrane to overcome the osmotic pressure that resists the flow of water. Since ultrafiltration and reverse osmosis involve no evaporation of water, energy consumption is much lower than in concentration by heating.

Fermentation of cereal grains and sugar crops for ethanol and use of reverse osmosis and ultrafiltration to process stillage solubles have been described (Wu, 1986, 1987; Wu and Sexson, 1984; Wu et al., 1981, 1984; Wu and Bagby, 1987). Fermentation of oats for ethanol and characterization of the protein-rich oat fermentation residue have not been described, however. This paper reports fermentation of ground whole oats, ground oat groats, and oat flour to ethanol, fractionation and characterization of the stillage, and use of reverse osmosis (RO) and ultrafiltra-