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Excretion of Triclopyr Herbicide in the Bovine

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Triclopyr, (3,5,6-trichloro-2-pyridinyloxyacetic acid) is a herbicide for control of woody plants and broad leaf weeds on rights-of-way, forests, industrial sites and turfs. A number of reports in the news media and legal literature (Lehoczky 1986) have associated application of Triclopyr and certain other herbicides near farm land with toxicity and death of cattle. Triclopyr has similarities in chemical structure and herbicide properties to Picloram (4-amino-3,5,6-trichloropicolinic acid) and sometimes the two herbicides are applied as a mixture. In an earlier study, it was shown that when Picloram was fed to a lactating dairy cow, 97.7% was excreted intact in the urine (Fisher et al. 1965). It was of interest to determine the mode of excretion of Triclopyr herbicide in the bovine. In the work reported here, Triclopyr was fed to a catherized, lactating dairy cow and milk, urine and feces were collected and analyzed for residues of the herbicide.

MATERIALS AND METHODS

A lactating Holstein cow weighing 630 kg was catherized and fed Triclopyr at the 5 ppm level based on a daily ration of 22.7 kg for four days. The pure herbicide in acetone was mixed with the grain. Milk, urine and feces were collected one day prior tofeeding the herbicide (control samples), daily throughout the feeding period and for six days thereafter.

The herbicide was extracted from milk, urine and feces by blending 25 grams of the sample with 60 ml of acetone and 1 ml of orthophosphoric acid for 3 minutes. The mixture was filtered and the filter was rinsed with acetone to a total volume of 100 ml. Five ml of the filtrate was partitioned with 5 ml of methylene chloride and 90 ml of 2% sodium sulfate. The methylene chloride was partitioned with 10 ml of 0.25 M sodium bicarbonate. The latter solution was acidified with 1 ml of concentrated hydrochloric acid and partitioned twice with 5 ml of methylene chloride. One ml of the combined methylene chloride extracts was methylated by the procedure of Schlenk and Gellerman (1960).

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Determination of Triclopyr was performed by gas chromatography using a Perkin Elmer Model Sigma 3B instrument equipped with a nickel-63 electron capture detector. A fused silica capillary column was used, 10 meters long, 0.53 mm i.d. and containing bonded methyl silicone 5µ in thickness. The temperatures of the column, flash heater and detector, respectively, were 175, 200 and 350°C with nitrogen (7cc/min) as the carrier gas. The limit of detection of Triclopyr in the samples was about 4 ppb on a fresh weight basis. The presence of Triclopyr was verified utilizing total and selected ion monitoring mass spectrometry. This was performed using a Hewlett Packard Model 5790 mass selective detector equipped with a 0.2 mm x 12 meter methyl silicone capillary column. All spectra were obtained using electron impact at 70 ev ionization energy. The capillary column temperature conditions were 130°C for 1 minute followed by a 15°C/minute rise to 280°C and then maintaining that temperature for 10 minutes. The retention time for Triclopyr was 4.6 minutes.

RESULTS AND DISCUSSION

Residues of Triclopyr were not detectable in the milk or feces samples. Based on the total quantity of the herbicide which the cow received during the four day period of dosing (454.4 mg), 86.4% was excreted intact in the urine. Daily mg totals of Triclopyr excreted during the first 5 days of the feeding trial were, progressively, 80.8, 94.9, 110.2, 102.8 and 4.0. Excretion of Triclopyr in the urine in this study may indeed have represented virtually the entire dose as was the case with Picloram (Fisher et al. 1965) but considering the large volumes of urine produced and the extreme sensitivity of the analytical methods, dilution errors may have prevented verification of this. None was detectable in the urine later than 24 hours after dosing ended on the fourth day. In Figure 1, the mass spectral data are shown from top to bottom, respectively, for the cow urine sampled on the third day of feeding Triclopyr, control urine and pure Triclopyr standard. Total ion chromatograms and fragmentation patterns are shown, respectively, in the lower and upper portions of each of the latter three samples in the figure. Notably abundant fragment ions are the 3,5,6-trichloro-2-pyridinyl(M/Z = 181.8), the molecular ion minus $C(O)OCH_3$ (M/Z = 209.8), the molecular ion minus OCH_3 (M/Z = 236.8) and the molecular ion (M/Z = 268.0).

The extracted ion profile for the above fragment ions are shown in Figure 2 representing, top to bottom respectively, the cow urine sampled on the third day of feeding Triclopyr, the control urine and pure Triclopyr standard.

Triclopyr is rapidly transported in the xylem and phloem of the honey mesquite plant when treated with the herbicide as the ethylene glycol butyl ether ester or amine salt formulation (Bovey et al. 1983). In studies with Triclopyr applied to moist soil columns, the intact herbicide and its metabolites, 3,5,6-trichloro-2-pyridinol and 2-methoxy-3,5,6-trichloropyridine were

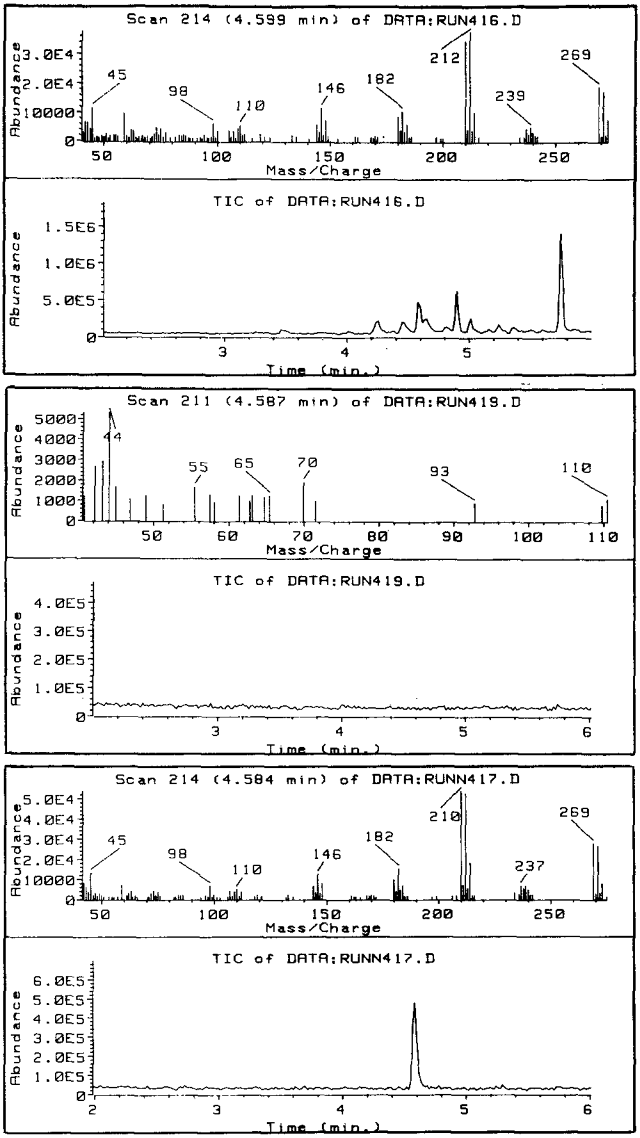

Figure 1. Total ion chromatograms (lower) and fragmentation patterns (upper) for, top to bottom, respectively, cow urine sampled on the third day of feeding Triclopyr, control urine and Triclopyr standard (see text for details).

found as 5, 85 and 10%, respectively, of the original quantity of herbicide applied after 54 days and these were confined to the top 10 cm of the soil column (Lee et al. 1986). These findings could be important since farm animals inadvertently ingest appreciable quantities of surface soil during grazing. A study was conducted in which horses were given nasogastric doses of Triclopyr as the acid equal to 5 times their estimated maximal field intake for the

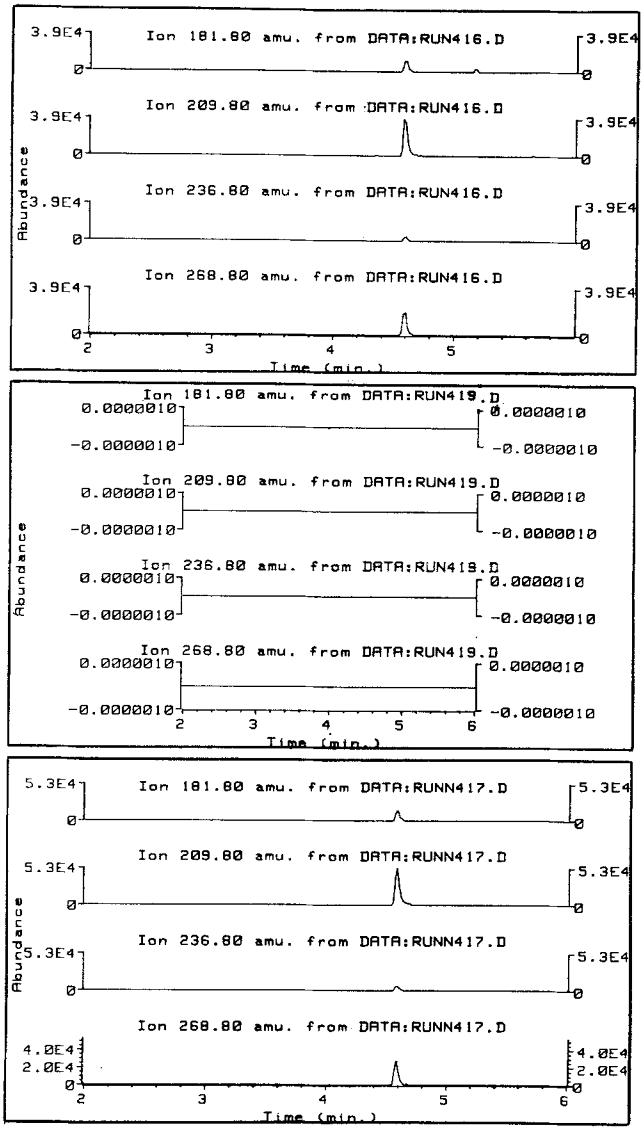

Figure 2. Extracted ion profiles for top to bottom, respectively, cow urine sampled on the third day of feeding Triclopyr, control urine and Triclopyr standard.

highest recommended usage rate as an herbicide (Osweiler 1983). Although a number of symptoms of toxicity and organ lesions were observed the author concluded that acute poisoning from proper use of the herbicide was unlikely. In studies with pregnant rats and rabbits in which Triclopyr acid was administered by gavage, little or no potential for teratogenic or reproductive toxicity was observed even when the level of exposure approached that which caused maternal toxicity (Hanley et al. 1984). It may be that any real association between cattle toxicity and field use of Triclopyr may well involve gross misuse of the formulated herbicide leading to exaggerated exposure levels in the animals. No external signs of toxicity were seen in the cow fed in this study.

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