Picloram Residues in Sprayed Macdonald-Cartier Freeway Right-of-Way

George J. Sirons,[1] Richard Frank,[1] and Ralph M. Dell[2]
[1]*Provincial Pesticide Residue Testing Laboratory, Ontario Ministry of Agriculture and Food*
Guelph, Ontario, N1G 2W1, Canada
[2]*Chief Arboriculturist, Ontario Ministry of Transportation and Communications*
Toronto, Ontario, Canada

The persistence and movement of picloram (4-amino-3,5,6-trichloropicolinic acid) applied to the median and the shoulders of a major highway were investigated. The herbicide formulation (Tordon^{R}101) was mixed with a particulating agent Norbak^R and applied over a 7-year period to the right-of-way of the Macdonald-Cartier Freeway, Ontario. Soil cores and grass samples were analyzed twice during each summer from seven locations. Under the climatic conditions of south western Ontario picloram began to move vertically down the soil profile immediately after application. Within 12 months picloram was substantially dispersed and after 30 months it was sufficiently diluted to exist only as a trace. Under the conditions of the experiment, lateral movement was not observed. It was concluded that picloram applied at rates up to 350 grams active ingredient per hectare every three years does not build-up in the top fifty centimeters of soil.

INTRODUCTION

This study was undertaken to investigate the cause of mortality of trees and shrubs in the vicinity where picloram had been applied to highway right-of-ways. The available field data about picloram persistence have originated either in the United States or Canada's prairie provinces and obviously are not applicable to the climate of southern and central Ontario where the damaged trees were observed. The investigation was carried out jointly with the Ontario Ministry of Transportation and Communications (OMTC) and the Ontario Ministry of Agriculture and Food (OMAF). The Macdonald-Cartier Freeway was the experimental site because it traversed the affected area located between 79° and 83° longitudinal and 42°-44° latitudinal coordinates. During the time of the experiment the temperature and precipitation averages did not diverge from the long term conditions (ANON. 1971 and ANON. 1968-1975). The study lasted 7 years (1968-1975) and consisted of two parts: the first (1968-1972) involved the establishment of the picloram residue levels at seven locations, while the second period (1973-1975) was confirmatory with samples being gathered at one site only.

MATERIALS AND METHODS

Application procedure: The formulation Tordon^{R}101 contains 62.4 grams (acid equivalent) of picloram and 250.8 grams (acid equivalent) of 2,4-D per liter, both present as the triisopropanolamine salts. It was applied to the median and the shoulder areas of the Macdonald-

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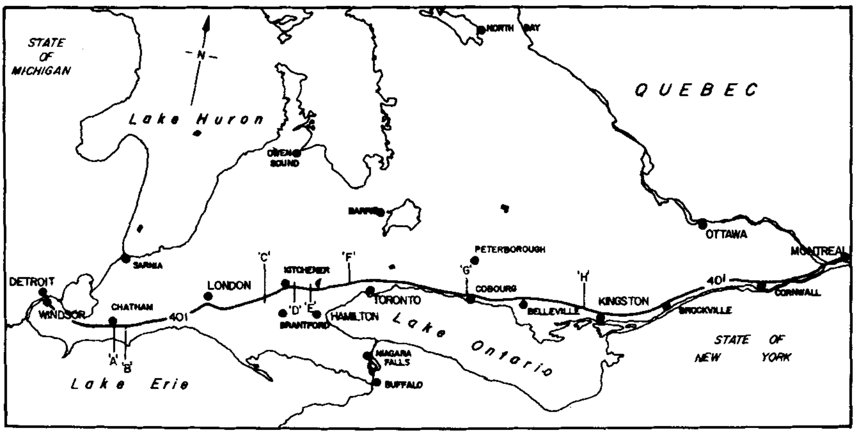
Cartier Freeway in alternate years beginning in May, 1968. The rate of application was 5.6 liters of Tordon 101 or 350 grams of picloram per hectare. To ensure that the herbicides were deposited only in the target area a particulating agent Norbak^R was added to the spray solution. Norbak consists of water-swellable, water-insoluble polymer particles (BYRD, B.D., et al 1971). The application was made by specially designed sprayers. To 4546 liters (1000 gal) water in a spray tank were added 113.6 liters of Tordon 101 and approximately 34 kg of Norbak. The mixture measured 57 sec/liter flow rate by OMTC standard funnel test. The viscous spray solution was dispersed through OC150 spray nozzles at 276 kPa (40 psi) head pressure. The spray vehicle was travelling at 20.9 km/hour during the spraying and the resulting application rate was 224.5 liters.

Sampling procedure: The original soil cores were 45 cm long and 6.35 cm in diameter and were obtained at locations of 72, 95, 241, 277, 322, 459, and 579 kilometers from the start of the Macdonald-Cartier Freeway at Windsor, Ontario (Fig. 1). The sampling commenced in May, 1969 and continued for 3 years with the samples being taken at the same distance and locations.

FIGURE No. 1



KEY MAP OF SOUTHERN ONTARIO

—— MACDONALD - CARTIER FREEWAY (401)

'A' - SAMPLE STATION 72 Km. (45 Mi.)
'B' - SAMPLE STATION 95 Km. (59 Mi.)
'C' - SAMPLE STATION 241 Km. (150 Mi.)
'D' - SAMPLE STATION 277 Km. (172 Mi.)
'E' - SAMPLE STATION 293 Km. (182 Mi.)
'F' - SAMPLE STATION 322 Km. (200 Mi.)
'G' - SAMPLE STATION 459 Km. (285 Mi.)
'H' - SAMPLE STATION 580 Km. (360 Mi.)

The soil cores were obtained by driving 6.35 cm diameter Shelby tubes into the ground to a depth of approximately 51 cm. The tubes were then removed from the ground with the core inside the tube, identified and coded, and returned to the OMTC laboratory. The core was extracted from the tube with a hydraulic ram, wrapped in aluminum paper, and delivered to the Provincial Pesticide Residue Testing Laboratory (OMAF) for analysis (Fig. 2).

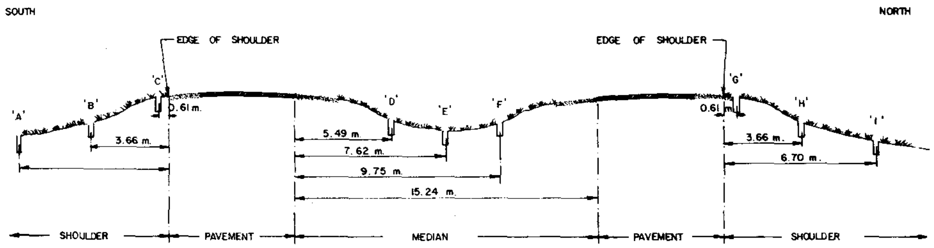


FIG. 2 (NOT TO SCALE)

In 1971 grass clippings were taken from the same sites as the soil cores. The grass was cut within a 45 cm diameter circle around the soil sample. Sampling for the second series of experiments began June 12, 1973, a few days before spraying (June 14, 1973) and ended October 29, 1975. The sampling was carried out to a depth of 30 cm using a 5.1-cm diameter by 15-cm long auger. The samples were dried by exposing to air for a few days and stored in a freezer at -20°C until analyzed.

During the seven years of the study 462 soil and 116 grass samples were analyzed for picloram. The soil samples taken from the median were largely clays and clay loams while those on the shoulders were mainly sandy loam with a few samples of the sandy and clay loam variety. Wide differences in soil texture were observed when sampling a transit across from the south shoulder to the north shoulders of a road section. These fluctuations in soil texture at points on the highway resulted in considerable variation in picloram residues from one core to another even when sampling sites were only a few feet apart.

Analytical procedure: Fifty grams of soil or 10 g of dried, ground plant material (grass) was weighed into a 250 ml Erlenmeyer flask and 150 ml of 0.1 N KOH in 10% KCl was added. While being stirred the mixture was heated almost to boiling, then placed into a water bath at 60°C and agitated for 20 min. The digested sample was centrifuged for 5 min. at 1500 rpm and the supernatant was decanted into a graduated flask. The sediment was re-extracted with 50 ml of 0.1 N KOH in 10% KCl as described above and the second supernatant was added to the first. From the extract a 100-ml aliquot was transferred to a 250-ml separatory funnel and gently washed with 50 ml of ethyl acetate. The ethyl acetate layer was discarded and the aqueous phase was acidified with 3 ml of dil. sulfuric acid (1:1). Twenty grams of NaCl was added and the water phase extracted twice with 50 ml of diethyl ether. The ether extract was dried by passing through anhydrous Na_2SO_4 and evaporated to dryness on a rotary evaporator (THE DOW CHEMICAL COMPANY 1968; GROVER, R., and L.A. KERR 1972).

The picloram residue was esterified by dissolving it in 3 ml of boron trifluoride in methanol (14%) and placing into a boiling water bath under reflux for 4 minutes. The esterified sample was transferred into a 60 ml sep. funnel using 30 ml of benzene. Twenty ml of water was added and the mixture was shaken for 30 seconds. After separation, the aqueous phase was discarded and the benzene extract was dried by passing through anhydrous Na_2SO_4.

The esterified soil extracts were purified by column chromatography using Woelm's basic alumina (Grade V with 15% water). The 10-cm high column packed in a 19 x 300 mm chromatography tube was prewashed with 25 ml benzene. The sample was percolated through the column followed by 100 ml benzene. The total benzene eluate was collected into a 250 ml boiling flask, evaporated on a rotary evaporator down to a few milliliters, then transferred to a graduated test tube and adjusted to volume with benzene.

For plant material an additional cleanup was necessary due to interferences of moderately volatile electron capturing compounds. Into a 19 x 300 mm chromatography tube with a Teflon stopcock activated Florisil was poured 10 cm high, then topped with a 2.5-cm layer of anhydrous Na_2SO_4. The column was prewashed with 50 ml of methylene chloride, which was removed with two 50 ml portions of petroleum ether. The methylated sample was transferred onto the column using 2 x 5 ml of benzene. After the sample penetrated, the column was washed with 100 ml of diethyl ether methylene chloride mixture (1:1). The picloram methyl ester was then eluted with 150 ml of 10% methanol in CH_2Cl_2, the eluate was evaporated on a rotary evaporator almost to dryness, transferred into a graduated test tube and adjusted to volume with benzene.

To expedite the analysis for the samples collected in 1974 and 1975 the esterification procedure was changed. The dry sample extract was esterified using 4 ml of diazomethane solution in diethyl ether at room temperature (20°C). After 20 min. the excess diazomethane and ether was evaporated with an air stream and the residue was dissolved in 10 ml benzene.

Quantitation was done by gas-liquid chromatography comparing peak heights with a standard curve obtained from analyzing fortified soil and plant samples.

The gas chromatographs used were: Varian Aerograph models 1200 and 1400, equipped with electron affinity (H^3) detection systems.

The chromatographic conditions were: Pyrex glass column, 0.32 cm o.d. x 183 cm packed with 5% Carbowax 20M on 60-80 mesh Varaport 30. Operating termperatures were: injector, 245°C; oven, 210°C; detector, 220°C. The carrier gas was purified nitrogen at 50 ml/min. Results were confirmed on a Tracor 550 gas chromatograph equipped with a Coulson electro-conductivity detection system operated in the nitrogen mode. Chromatographic conditions were: Pyrex glass column, 0.64 cm o.d. x 183 cm packed with 5% OV17 on 80-100 mesh Gas Chrom. Q.; operating temperatures were: injector, 210°C; column, 190°C; transfer line, 210°C; pyrolyzer, 860°C. The carrier gas was helium at 50 ml/min.

Reduction was carried out in a 0.64-cm o.d. x 30-cm quartz tube containing a nickel wire catalyst and a strontium hydroxide scrubber. Water flow through the conductivity cell was at a rate of 3 ml/min (approx.) and was purified by an ion exchange resin consisting of a 15 cm Duolite ARA-366 (OH^-) column topped with 2.5 cm Bio-Rad AG 50W x 8 (H^+), both 20-50 mesh.

The excellent sensitivity for picloram with an electron capture detection system (0.001 ppm or 0.1 ng for 50% FSD) is not achieved using the Coulson type electro-conductivity cell; however, large injections (50 µl) and specificity compensate for this disadvantage. The response for picloram at the above described conditions was 0.01 ppm or 5 ng for 50% FSD. The recoveries varied between 70 and 90%. In order to minimize the possibility of errors due to irreversible adsorption of picloram during sample storage, quantitations were based on standard curves obtained from control soil samples which were fortified with picloram at the time that the respective analysis programs began.

DISCUSSION AND CONCLUSIONS

In this investigation the sprayed herbicides were exposed to conditions which are not encountered under normal field applications. First the Macdonald-Cartier Freeway is a 4-lane highway designed to maintain a definite moisture level in its road bed, while the surface water is quickly drained. Second, to ensure against drifting, a thickening agent (Norbak) was used. In a similar experiment conducted by Dow Chemical Company (BYRD, B.D., <u>et al</u> 1971; GORING, C.A.I., and J.W. HAMAKER 1971) the vertical movement of picloram was proportional to the slope of the soil profile, to the precipitation, and as much as 50% of applied herbicide was retained by vegetation. The same factors had a definite bearing on residue levels found in the shoulder of Macdonald-Cartier Freeway. The road shoulders, at each sampling location, were of different soil types affecting adsorption and making comparisons difficult. The median, on the other hand, was uniformly clay or clay loam. Correspondingly the results of the median soils show a definite pattern. On both sides of the median the middle portion retained the picloram for a longer period of time than the top or the bottom. This indicates that the gravel drainage at the pavement edge (Fig. 2a, sites A and E) as well as the ditch line created a water course which hastened the picloram washout. The fact that picloram did not accumulate at any particular location indicates that lateral movement of the herbicide is limited. In this respect our results are in line with the findings of Suffling, R.,

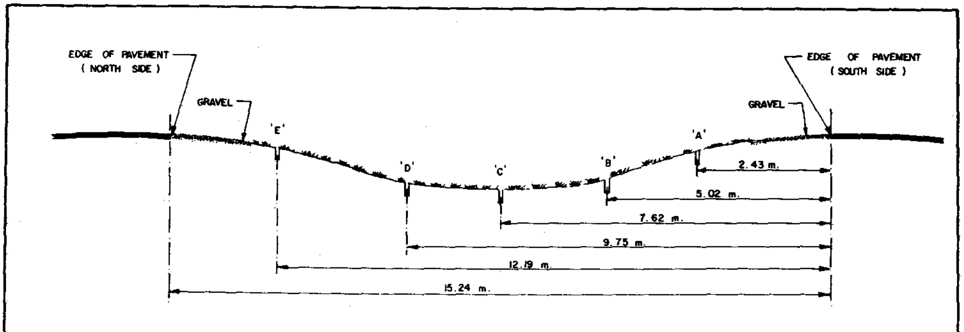


FIG. 2a (NOT TO SCALE)

et al (1974). Finally, the retention and uptake of picloram by the vegetative cover was very pronounced.

The compiled results demonstrate that picloram applied as the triisopropanolamine salt is highly mobile vertically. Within a year it became diluted and, due to the low concentrations and adsorption on the organic matter, lost its phytotoxicity (ASSOC. COMMITTEE ON SCIENTIFIC CRITERIA FOR ENVIRONMENTAL QUALITY 1974). In the case where picloram would be applied in alternate years the levels would slowly rise and eventually endanger the shrubs and trees growing nearby. A three year application cycle would be adequate for brush control and would not contaminate the surrounding area (Table 1, Fig. 3).

Fig. 3

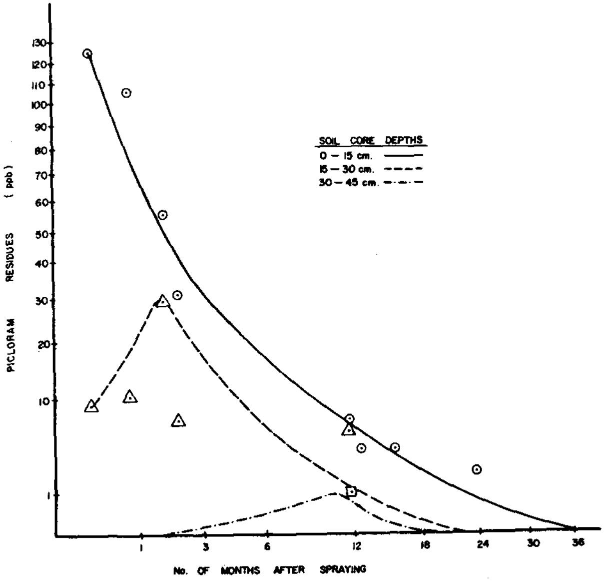


TABLE 1

Residues of picloram following the spraying of highway shoulders and medians with picloram between 1968-1973

km Marker	Sampling, # of months after spraying	Picloram residues (ppb) in air dried samples Soil core depths (cm) 0-15	15-30	30-45	Picloram in dried grass (ppm)
72,95,95,293, 459,579	0.2	124.8	8.9	ND	15.7
277,277,293, 322	0.6	105.3	10.4	TR	12.6
92,241,293	1.6	55.5	30.0	TR	29.8
72,95,95,241, 241,277,277, 459,579	2.1	31.0	7.4	0.1	0.9
72,277,293, 293,322	11.6	7.5	6.6	1.4	1.6
72,241,241	12.5	4.5	TR	TR	0.3
72,293	15.4	4.0	TR	TR	0.2
241,277,293, 293,459,579	23.6	2.5	TR	TR	0.1
72,293,293	27.4	TR	ND	ND	TR
72,95	36.0	ND	ND	ND	ND

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