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THE PERSISTENCE, BREAKDOWN AND MOVEMENT IN SOIL OF THE

HERBICIDE TRICLOPYR (3,5,6-TRICHLORO-2-PYRIDYLOXYACETIC ACID)

AND ITS ETHYLENEGLYCOLBUTYLETHER ESTER

by

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B. Sc. (Hons), University of Malaya, 1979

PROFESSIONAL PAPER SUBMITTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

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of

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                                    pyridyloxyacetic acid) and its ethyleneglycolbutylether
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The persistence, breakdown and movement in soil of the herbicide

triclopyr (3,5,6-trichloro-2-pyridyloxyacetic acid) and its

ethyleneglycolbutylether ester.

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ABSTRACT

Garlon® is the trade name of several herbicides whose active ingredient is triclopyr (T) (3,5,6-trichloro-2-pyridyloxyacetic acid). The commercial product Garlon® 4 contains T as the ethyleneglycolbutylether ester (EGBE). Relevant aspects of the behaviour of technical T and EGBE in a soil representative of British Columbia coastal forest (34% org. matter, 8.3% clay, pH 3.4) were studied in the laboratory. T or Garlon® 4 were applied to the tops of individual columns of the soil at a rate equivalent to 5 lb/acre of T. Every second day, for 54 days, water equivalent to 2.5 cm of rainfall was added slowly to the top of each column and the resultant eluate collected for analysis. Columns of sand were treated similarly. Finally, each column was divided into four equal sections. The eluates and soils were analysed by a method developed for T, EGBE, and the two metabolites, 3,5,6-trichloro-2-pyridinol (TP) and 2-methoxy-3,5,6-trichloropyridine (MTP).

No movement of residues within, or through the soil could be detected: only the top sections contained residues, namely low concentrations of T and MTP, and high concentrations of TP, representing, respectively, about 5, 10 and 85 % of the total recovered, which was approximately 60% of the amount applied originally to the top of each soil column. No EGBE was detected.

By contrast, residues moved through the sand readily. After treatment with EGBE, all residues passed through the sand in 34 days of leaching and were recovered in the eluates,

quantitatively, in the form of T, except traces of EGBE and TP, suggesting complete hydrolysis of EGBE to T without further break-down of T. After treatment with T, 65% of the applied T had leached through the sand in 54 days, and 10% were found in the four sections of each sand column, about 25% had probably been converted to compounds not detected. The faster movement of the residues through sand after treatment with Garlon® 4, an emulsifiable concentrate, was probably caused by surfactants in the formulation.

Based on the results, a pathway of degradation of EGBE has been proposed. It was further concluded that the probability is high that T and EGBE will neither persist nor move vertically with water in soils of B. C. coastal forests and that leaching through such soils into sub-surface water, with subsequent transport into fish-bearing aquatic environs, is unlikely to pose a hazard in the field if the herbicide is used properly.

DEDICATION

To my wife, Lee Chia; and

my children, Chee Eng; Chee Hoong, Lay Chin; for

without their patience, understanding, love and

sacrifice of time, this thesis would not have materialised.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

The needs of the world call for the utilization of all available scientific technology to produce and protect high-value food, forage and fiber crops. Weed control is an essential part of this vital process. For centuries, traditional methods of weed control, such as tilling and hoeing, have been used; but these have become economically inefficient. In many cases, crops that could be grown were dictated by the weeds present and the best weedkiller then was a good crop (Saka, 1983).

The use of herbicides, chemicals that kill plants or inhibit their normal growth, together with improved crop varieties and fertilisers, brought about a change in this pattern of life. It accelerated with the discovery of 2,4-D (2,4-dichlorophenoxyacetic acid) and MCPA (2-methyl-4-chlorophenoxyacetic acid) in the 1940's. These chemicals have hormonal effects similar to auxins, and are highly effective at low dosages (<1.0 kg/ha). Earlier compounds, such as sulphuric acid, DNOC or sodium arsenite, can be highly toxic or hazardous to use, but 2,4-D and MCPA are easier and safer to use and handle. Subsequently, 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) and other new groups of chemicals, including the picolinic acids, e.g. picloram (4-amino-3,5,6-trichloropicolinic acid) were developed.

The high selectivity of these herbicides against broad-leaved weeds and woody plants has brought about a revolution in agriculture, forestry, recreational land use, and vegetation management on rights-of-way. Herbicide applications, especially in forestry, have been made with small aircraft or helicopters depending on area size and terrain. Under such circumstances, herbicides are applied as foliar sprays to achieve uniform coverage and even distribution. With the advent of these herbicides, weeds that were serious problems in many countries, such as New Zealand (MacDiarmid, 1977), the United States (Haagsma, 1975; Howard et al., 1983), England (McCavish, 1980) and Japan (Saka, 1983), could be controlled.

In the 1960's, even though picloram was available, the phenoxy herbicides remained the primary means of perennial weed control because picloram is more persistent in soils and therefore unsuitable for use in reforestation (Gratkowski, 1978) and crop lands (Saka, 1983). In areas with tree and brush species not susceptible to phenoxy herbicides, effective control was attained with picloram and picloram-phenoxy mixtures, applied to the base of the plants or as trunk injections to avoid possible problems from its persistence in soils (Lauterbach and Warren, 1982; Voeller et al., 1976). Despite its effectiveness, some hardwood species were able to resprout (Radosevich et al., 1976), so that control of unwanted plants, not susceptible to phenoxy herbicides, in steep terrain and remote, inaccessible areas was difficult to achieve (Fears and

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Dickens, 1978). Thus, there was a continued need for foliage-applied herbicides, especially when 2,4,5-T was banned from use in the US in 1979. The use of 2,4,5-T was subsequently banned by other countries also, including Norway (McCavish, 1980) and Finland (Siltanen et al., 1981).

In Canada, 2,4,5-T although still registered for forestry use federally[1], has not been in operational use in most provinces for the last couple of years because of the controversies over it. 2,4-D is the frequently used herbicide. In addition, glyphosate and hexazinone (temporarily) are also made available. However, these 3 herbicides available are considered inadequate to address the full range of grass, weed and undesirable brush problems across Canada (Green, 1984).

The need for alternative new and effective herbicides is not only caused by these factors but also by regular increases in labour costs, which make manual control of weeds prohibitive. Compounded by other aspects of inflation, these deplete available land management funds (Gratkowski, 1978). New herbicides should not only be more effective and less costly than those currently available, but also environmentally acceptable. Most compounds applied will inevitably find their way into the soil and water. The use of herbicides is also greatly influenced by their fate and behaviour in the soil (Klingman et al., 1982).

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[1] no further registration renewal from 1st January 1985

The fate and behaviour, such as movement and chemical changes, of a pesticide in soils are influenced by several factors (Bailey and White, 1970), of prime importance among them is adsorption (Khan, 1980).

Adsorption, the chemical and physical attraction of a pesticide to the specific surfaces of soils (Bailey and White, 1970) is significantly influenced by the chemical nature of the herbicide and the soil type (Klingman, et al., 1982). For herbicides, for instance, hydrophobicity, pK values of ionizable groups, and the capacity for hydrogen bonding are important features in sorption (Khan, 1980). In soils, components of importance are clay and organic matter. Soils with organic matter content of <6% have both mineral and organic matter involved in adsorption (Walker and Crawford, 1968; quoted by Stevenson, 1976). In soils with >6% organic matter content, adsorption occurs mostly to organic surfaces. Clays (crystalline minerals, crystalline and amorphous oxides and hydroxides, and montmorillonite and kaolinite) would affect adsorption by differences in surface area availability and cation exchange capacity.

Organic matter, comprising humic substances (humin, humic acid and fulvic acid) and non-humic substances (carbohydrates, proteins and other organic acids of low molecular weight), may act as surfactants or adsorbants (Wershaw et al., 1969). Adsorption may be by van der Waals forces of attraction, hydrophobic bonding, hydrogen bonding, electrostatic attraction,

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ion and ligand exchange (Khan, 1980). Humic and fulvic acids being rich in functional groups, may bind pesticides, while the non-humic fraction may facilitate microbial breakdown of pesticides (Khan, 1980).

Movement occurs primarily by leaching, runoff and volatilization. Information on movement is essential for predicting potential contamination of other environments. Leaching can transport pesticides to ground water, eventually contaminating other water bodies and systems. It is affected by factors such as soil profile, flow rates and amounts of soil water. In general, there is an inverse relationship between adsorption and movement of pesticide by water through soil (Khan, 1980).

Chemical changes of a pesticide in soil include metabolic and non-metabolic conversions. The former are bio-transformations, mostly by microorganisms, whereas the latter can be catalysed by clay surfaces, metallic oxides, ions and organic matter. A site of high biological and non-biological activity is the humus-clay microenvironment (Khan, 1974).

Persistence of a pesticide in a soil is directly related to its chemical stability and adsorption. It is inversely related to rates of leaching and decomposition, processes which result in a decline of the pesticide.

Among recently developed herbicides that are applied to foliage and have potential for control of broad-leaved weeds and woody brush is triclopyr (3,5,6-trichloro-2-pyridyloxyacetic

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acid). It is of low toxicity to warm-blooded animals (acute oral LD_{50}, rats, 713 mg/kg) and of moderate toxicity to trout and bluegills with 96-h LC_{50} of 117 ppm and 148 ppm, respectively (Spencer, 1982). It is known to break down to 3,5,6-trichloro-2-pyridinol (McKellar et al., 1982), a compound which, although not toxic to mammals (Roberts and Marshall, 1978), may nevertheless be toxic to fish. Another possible metabolite in soil could be 2-methoxy-3,5,6-trichloropyridine, whose toxicity is not known. Although a candidate for use in forestry in British Columbia and Eastern Canada, little information exists about its persistence, breakdown and movement in soils. As nothing of its fate and behaviour in the soils of the forested regions of British Columbia is known, the present study was undertaken with the following objectives:

1. To study the propensity of triclopyr (T) to move through a forest soil following applications to the soil in the laboratory of:

   a. technical T and

   b. Garlon® 4, an emulsifiable concentrate, containing ethyleneglycolbutylether ester (EGBE) of T.

2. To investigate the formation and movement of two metabolites, 3,5,6-trichloro-2-pyridinol (TP) and 2-methoxy-3,5,6-trichloropyridine (MTP).

3. To develop suitable methods of analysis for this study.

II. LITERATURE REVIEW

Triclopyr and Its Formulation

Triclopyr is the common or generic name for 3,5,6-trichloro-2-pyridyloxyacetic acid. Its empirical formula is $C_7H_4Cl_3NO_3$ and its molecular weight is 256.5 (Fig. 1).
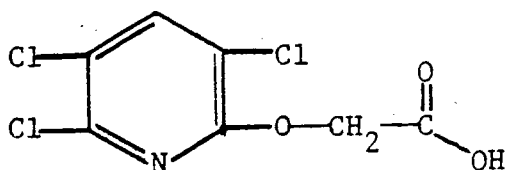
Figure 1. Structure of Triclopyr (3,5,6-trichloro-2-pyridyloxyacetic acid).

It is a relatively new herbicide that was introduced by The Dow Chemical Company in 1970 (Spencer, 1982). It is available commercially as aqueous triethylamine, a water-soluble formulation containing 3 lbs/gal., or as ethyleneglycolbutylether ester, a solvent-based emulsifiable concentrate containing 4 lbs/gal. Most studies have reported the ester formulation to be more effective than the amine (Lichy,

1978; Forgie et al., 1977; Howard et al., 1983; Jacoby and
Meadors, 1983). However, Reynolds et al. (1983b), reported the
opposite for controlling various large mesophytic trees.
Unfortunately, it was found that they had applied less triclopyr
as the ester than as the amine.

Uses of Triclopyr

a. Weed control in Forestry and on Rights-of-Way

Studies indicated as early as 1972 and 1973 that triclopyr
had excellent herbicidal activity against a broad range of woody
plants (Byrd et al., 1974). Hardwood species, such as ash,
cherry and oak, can be effectively controlled (90-100%) by high
volume applications of 1 - 2 lbs/acre[1],[2] in 100 gallons[3] of
spray mixture (Byrd et al., 1975; Lichy, 1978). A high degree of
consistency in control was attained at more than 51 sites tested
in the United States. For some species, such as blackberry,
yellow poplar and salal, 3 - 4 lbs/acre were required (Byrd and
Colby, 1978). To control maple, aspen, birch and some others,
rates of 6 - 9 lbs/acre were necessary.

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[1]Rates expressed as triclopyr (= active ingredient = acid
equivalent) throughout this paper

[2]lb/acre X 1.12 = kg/ha

[3]1 gal = 3.8L

With the application of 1 - 2 lbs/acre in 100 gallons of the spray mixture at which most hardwoods are controlled, the softwood conifers, Sitka spruce, hemlock and some pine species, were found to be relatively tolerant (McCavish, 1980). Western red cedar and balsam fir were found not to be affected at all (Byrd and Colby, 1978; Byrd et al., 1975). These results showed that triclopyr was of excellent potential for conifer release in forestry.

The effectiveness of triclopyr as a herbicide was compared with picloram and other phenoxy herbicides on trees and perennial weeds. According to Byrd et al., (1974) triclopyr was superior to 2,4,5-T, for it gave better control of a broad range of woody plants with lesser amounts required. Triclopyr was shown to provide effective control of trees (Haywood, 1980), such as golden evergreen chinkapins, canyon live oak (Gratkowski et al., 1978) and ash, where picloram and 2,4-D provided unsatisfactory control. Triclopyr was consistently effective even when applied under difficult conditions, such as steep terrain where applications of picloram would be economically prohibitive (Fears and Dickens, 1978). Against blackberry (Forgie et al. , 1981) and sweet brier (Bristol, 1981), triclopyr was more effective than 2,4,5-T.

Recent studies showed that triclopyr applied at <0.96 kg/ha was effective against red alder but not thimbleberry and black cottonwood (D'Anjou, 1985). As results on the latter were not encouraging, subsequent studies with higher rates, i. e. 1.5* -

3.0 kg/ha are anticipated. Triclopyr has also been reported to be effective for controlling large-diameter Appalachian hardwoods, such as maple and tulip (Reynolds et al., 1983a) and mixed, mesophytic trees, such as red oak and white ash (Reynolds et al., 1983b). Seasonal studies suggested that triclopyr applied during the dormant season could also kill trees, such as tupelo and tulip poplar (Reynolds et al., 1983c), thereby improving management capabilities and avoiding water bodies more easily. Triclopyr was also found to be a good preburn desiccator (Gratkowski et al., 1978).

b. Weed Control in Pasture and Crop Land

Triclopyr was effective against honey mesquite (Jacoby and Meadors, 1983), horsenettle (Gorrell et al., 1981), and tall ironweed (Mann et al., 1983). It was found to be as effective as VEL-4207, a derivative of dicamba, for the control of weeds in small grains, pastures and turf areas (Ketchersid and Merkle, 1978). Of all the available hormone-type herbicides, it was the most effective one for control of gorse (Rolston and Devantier, 1983). There were controversial reports regarding its effect on grasses for Byrd et al. (1975) reported temporary injury to established grasses whereas Bovey et al. (1984) found injury to common buffelgrass at rates as low as 0.6 kg/ha. However, it has also been suggested that triclopyr stimulated the growth of grasses, thereby enhancing its benefits on pastures (Reynolds et

al., 1983a). According to Gorrell et al. (1981), it would be superior to picloram, also, in corn production under minimum tillage.

On crop land, especially on pineapples, the use of 2,4-D and paraquat provided unsatisfactory weed control. Problems with resprouting, small-sized fruit and reduced yields were also encountered. However, triclopyr was more effective at lower cost (Lee et al., 1984). In rubber plantings, triclopyr was suggested as an alternative that could replace sodium arsenite and n-butyl ester of 2,4,5-T, which are used for killing standing trees and felled stumps (Lim and Abdul Aziz, 1981). In oil palm plantations, triclopyr has also been demonstrated to be highly effective for weed control, however, its use is considered to be uneconomical (Teoh et al., 1982). It offers potential for use in mixtures with grasskillers as a general herbicide (Anon., 1982).

Mode of action

Triclopyr was found to have effects on barley resembling those of indole-acetic-acid (IAA). Its shoot-to-root ratio (S/R) of 8.62, was comparable to 9.47 for picloram. These values were the highest of six related pyridine compounds tested, the S/R values of the others ranging from 0.66 to 1.55 (Foy and Chang, 1979).

Toxicity

Preliminary toxicological studies showed that triclopyr is of low toxicity to mammals (acute oral LD_{50}, rats, 713 mg/kg) and is not unduly dangerous if ingested and inhaled during handling and spraying. It is of low toxicity to birds (acute oral LD_{50}, Mallard duck, 1698 mg/kg) and of moderate toxicity to fish (96-h LC_{50}, trout, 117 ppm, bluegills, 148 ppm). The amine formulation is less toxic than triclopyr to mammals (acute oral LD_{50}, rats, 2140 mg/kg), fish (96-h LC_{50}, trout, 240 ppm, bluegills, 471 ppm) and birds (acute oral LD_{50}, Mallard duck, 3176 mg/kg). The ester formulation is also less toxic than triclopyr to mammals (acute oral LD_{50}, rats, 2140 mg/kg) and birds (acute oral LD_{50}, Mallard duck, 4640 mg/kg) but much more toxic to fish (96-h LC_{50}, trout, 0.74 ppm, bluegills, 0.87 ppm) (Weed Sci. Soc. Am., 1983). It is not known whether the toxicities (LD_{50}/LC_{50}) cited above were expressed on the basis of triclopyr or not. According to Gersich et al. (1984), concentrations in water of 336 to approx. 2,000 ppm caused 0 to 100% mortality of Daphnia magna. These concentrations were several orders of magnitude higher than those found in the environment by McKellar, et al. (1982), following an application rate of 10 kg/ha.

Uptake from soil into plants

According to King and Radosevich (1979b), absorption of aerially applied triclopyr through leaf surfaces was preferably by way of guard cells. Passage was hindered by wax, so that the uptake by immature leaves was greater than that of mature leaves because of a thinner wax layer on the former. Absorption was enhanced by the presence of stellate trichomes, and was found to be higher abaxially than adaxially (King and Radosevich, 1979a).

The uptake of triclopyr from soil was equivalent to or greater than that of picloram (Bovey et al., 1979). Higher levels of triclopyr in roots were found with soil than with foliar applications. In the latter, the uptake and accumulation of triclopyr by leaves was high. However with soil application, the uptake and accumulation was lower in leaves and stems than in roots, suggesting that there was either metabolic transformation or less efficient transport (Bovey et al., 1979). Movement of triclopyr to the leaves was highest with warm temperatures and long day photoperiods, indicating symplastic movement (Radosevich and Bayer, 1979). By radioactive labelling they showed that triclopyr was more mobile than 2,4,5-T.

Persistence and Degradation

Long-term studies (560 days) with an aerial application rate of 10 kg/ha indicated no significant movement from the site of application (McKellar et al., 1982). Water and soil samples collected from densely-wooded areas, on the day of application,

had no detectable levels of the herbicide. However, soil samples from slightly wooded areas had 4.4 ppm, and others from open areas had 18 ppm of triclopyr. In addition, 0.28 ppm of the metabolite, 3,5,6-trichloro-2-pyridinol, were noted on day 28. Torstensson and Stark (1982) also found that aerially applied triclopyr was retained mostly by the vegetation. However, with time they noted increases in herbicide levels in the soil, suggesting that it had washed off. In their soil analyses, they noted that triclopyr was more persistent than 2,4-D.

In the USA, Moseman and Merkle (1977) reported that triclopyr applied in the fall would persist for six months whereas application in summer would be completely dissipated in three months. In New Zealand, no residues were noted 3-4 months after application even when rates as high as 12 kg/ha were used (MacDiarmid, 1977).

These studies provided information on triclopyr pertinent to other countries. The present study was undertaken to obtain information, relevant to British Columbia, on the persistence and movement of triclopyr in a soil, and on its degradation. Of particular importance is the study of an ester formulation which seems to be preferred on account of its efficacy.

III. MATERIALS AND METHODS

Soil

Soil columns have been extensively used for the study of movement of pesticides in the laboratory (Wilson, 1973; Hogue et al., 1981). Based on this, the present study with soil and sand columns, similar to that described by Wilson (1973), was undertaken. The soil was collected from the top one metre, after the duff layer had been removed, in a virgin cedar-hemlock forest in the the wet coastal biogeoclimatical zone of British Columbia. It was from an area with predominantly Cannel type soil (Luttmerding, 1980). The collected soil was air-dried, passed through a No. 10 sieve (2mm openings) to remove large particles and mixed.

Prewashed and dried silica sand (Martin Marietta, Emmett, Idaho) passed through a No. 35 sieve (0.5mm openings) was used. Sand was used because it contained no clay and organic matter, the components mainly responsible for sorption of residues in soils.

Leaching apparatus

Glass columns (73 cm X 9 cm OD) were filled with sand or soil to a height of 40 cm. The contents of each respective column were held in place by a sheet of teflon mesh securely fastened to the outside of the base with silicone sealant and two broad rubber bands. The columns were clamped near the top and rested on glass funnels suspended in holes in a plank of plywood. Erlenmeyer flasks of 250-ml vol. were placed beneath the funnels to collect water eluted from the columns. Distilled water was applied to each column from an inverted 500-ml Erlenmeyer flask, stoppered by a cork with two glass tubes: one for pressure equalisation and the other for water release. A rubber tube and clamp were attached to the latter tube to regulate flow (Fig. 2). Ten columns were set up: 5 columns each of soil and sand. All columns were conditioned with 5 applications of 250 ml of distilled water for 5 days.

The laboratory had an average temperature of 21C (range 12-30C). Occasionally, low temperatures were recorded at night and highs at midday. The RH averaged 59% (range 20-98 %).

Herbicide

The herbicides used were technical T of 99.1% purity; and Garlon® 4, an emulsifiable concentrate, EPA (US) Reg. No. 464554, containing 61.6% EGBE (= 44.3% triclopyr equivalent = 0.48 kg per L = 4 lbs triclopyr equivalent per US gallon).

Figure 2. Experimental Set-up of a Soil
and Sand Column.
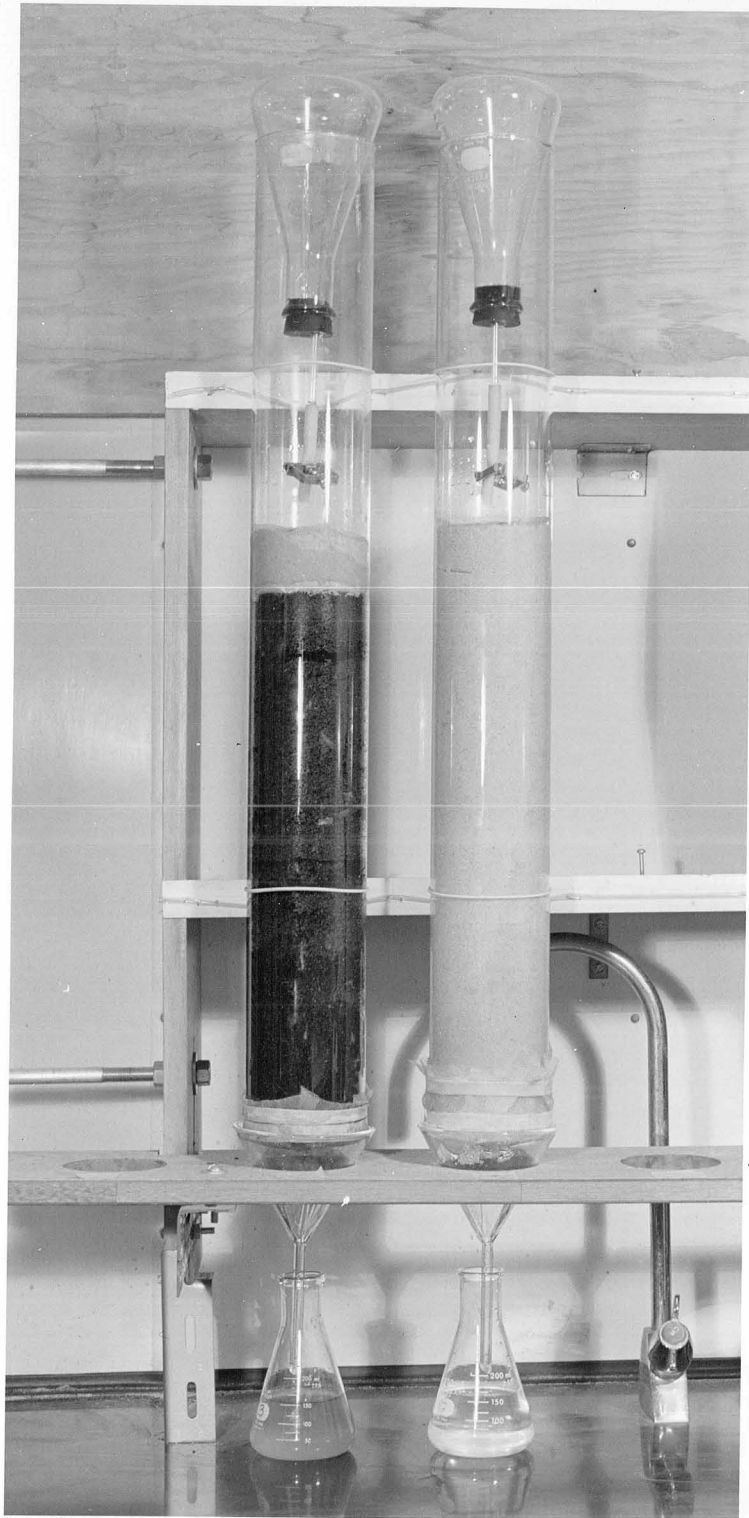
17b

Garlon® 4 is not registered in Canada under the Pest Control Products Act. For application to the soil or sand, technical T was dissolved in glass-distilled acetone and Garlon® 4 was diluted with the same solvent.

Treatment

Five samples of 100g each of soil (fresh weight) and of sand were weighed into Mason® glass jars and mechanically tumbled. Ten millilitres of 0.35 mg/ml of T and 0.51 mg/ml of Garlon® 4 (equivalent to 0.35 mg/ml of T) in acetone were respectively applied to four samples of sand and soil giving treatment levels of 35 ppm, equivalent to field application rates of 5.6 kg/ha (5 lbs/acre). The remaining sand and soil were used as controls, treated with 10 ml of acetone. The application was made by gradual injection of 5 ml of the appropriate solution, twice at five-minute intervals. The treated sand and soil were left to tumble for 1 h, to ensure even distribution of the herbicide and allow the acetone to evaporate.

Each 100g of treated sand or soil was added to the top of the respective columns, covering the non-treated sand or soil. A 9-cm Whatman #1 filter paper was placed on top of the treated layer. This was followed by another 5 cm of untreated sand and another disk of filter paper. The filter papers and sand layer were added to prevent channelling of the applied water. Details

are shown in Table 1.

Leaching procedure

Every second day, 160 ml of water (equivalent to 2.54 cm of rain) were applied at the rate of 2 ml/min. The resulting eluates were collected after 48 h and transferred into 200-ml dark glass bottles and stored at -20C. A total of 27 eluates per column was collected during 54 days of leaching. On completion of leaching the columns were wrapped with aluminium foil and stored at -20C until they were analysed. Extraction and cleanup of collected eluates were as described in the method of analysis (p22).

Removing frozen soil and sand from columns

Each frozen soil column was taken from the freezer and clamped onto a retort stand. The rubber bands securing the teflon mesh were first removed, then a sharp razor blade, rinsed with acetone, was used to scrape off the silicone sealant and hence to remove the teflon mesh from the base of the column. Paper towels soaked in warm water were applied around the sides of the column to speed up thawing of the soil adjacent to the glass surfaces and facilitate their separation.

A wooden rammer, covered with aluminium foil and cleaned with acetone, was pushed gently against the top of the soil

TABLE 1

Columns, Packings and Treatments of the Experiment.

Column	Packing [a/]	Treatment [b/]	Fortification [c/] (ug)
1	soil	control	0
2	soil	EGBE	3500
3	soil	EGBE	3500
4	soil	T	3500
5	soil	T	3500
6	sand	control	0
7	sand	EGBE	3500
8	sand	EGBE	3500
9	sand	T	3500
10	sand	T	3500

[a/] Soil: Cedar-Hemlock Forest Soil. Sand: Silica Sand.

[b/] EGBE: Ethyleneglycolbutylether Ester of Triclopyr.
T: Technical Triclopyr.

[c/] 100 g of Treated Packing (35 ppm), Applied to Top of each 40-cm Packing.

core. When there were signs of sliding, the core was pushed out onto a piece of clean aluminium foil. A hacksaw that had been cleaned with acetone was then used to saw the core into 4 sections, each about 10 cm long. The sections were labelled #1, 2, 3 and 4 from the top downwards. When thawing was complete, each section was thoroughly mixed and aliquots were removed for measuring moisture content and for pesticide analysis.

Sand cores could not be removed from the columns until they were completely thawed. The sand then slid out and was separated into four approximately equal sections.

Determining pH in eluates, soil and sand

The pH of soil or sand was determined by weighing duplicate samples of 25g into 250-ml beakers. About 25 ml of glass-distilled, deionised water were added to make a thin suspension which was stirred with a magnetic stirrer for 30 minutes. The pH was determined with a Radiometer®, Model 26, equipped with a glass calomel electrode. The same instrument was used to measure the pH of the water eluates.

Determining dry weights

Four soil samples, 50g each, were weighed onto Petri dishes and dried in an oven at 105C for four days. The soils were weighed on the 3rd and 4th days but not again, because the

weights were constant.

Extracting water eluates

Fifty millitres of each eluate were measured into a 250-ml separatory funnel. Ten drops of concentrated H_2SO_4 (sulphuric acid) were added to acidify the eluate to about pH 2. Each eluate was extracted three times with CH_2Cl_2 (dichloromethane), 50 ml for the first extraction and 25 ml for the second and third. During each extraction, the separatory funnel was shaken three times, about 1 min each time, followed by a release of pressure. The phases were allowed to separate between shakings.

After each extraction, the CH_2Cl_2 was put through a bed of anhydrous granular Na_2SO_4 (sodium sulphate) and collected in a 250-ml round-bottom flask. After the third extraction, a further 10 ml of CH_2Cl_2 was used to rinse the Na_2SO_4 bed.

Derivatizing

To a solution of 4 ml of water containing 2.5g of KOH (potassium hydroxide), were added 12.5 ml of 95% ethanol, in a 100-ml round-bottom flask. Simultanously, 10.75g of the diazalt, 99% N-methyl-N-nitroso-p- toluenesulfonamide, were dissolved in 100 ml of diethylether. The ethanolic-KOH solution was placed on a water bath. A drop funnel with a regulator knob and a condenser was connected to the round-bottom flask. At the

receiving end of the condenser was a conical flask maintained at
0C.

The water bath was held at 65C. The diazalt solution was
slowly added through the dropping funnel, to the round-bottom
flask containing the ethanol solution. The rate of distillation
was approximately equal to the rate of addition. The cooled
yellow solution, collected in the conical flask, contained the
diazomethane. All ground glass surfaces in the apparatus were
covered with teflon sleeves to prevent accidental explosions.
The procedure is as described by Maybury (1980).

The CH_2Cl_2 extracts of the eluates, about 110 ml in the
round-bottom flasks, were then flash-evaporated to just dryness
and the residues taken up in 1 ml of benzene. To each was added
about 1 ml of the methylating reagent, i. e. the freshly
prepared diazomethane, which was allowed to react for half an
hour, after which 10 drops of keeper (1% paraffin oil in hexane)
were added. Excess diazomethane was then driven off with a
stream of nitrogen gas.

As controls, 1-ml aliquots of T in benzene at
concentrations of 0.05, 1.0 and 10.0 ug/ml were placed in 250 ml
round-bottom flasks. The same was done with solutions of TP. To
each of these were added about 0.5 ml of freshly prepared
diazomethane and allowed to react for 30 min in the fume hood.
Then 10 drops of keeper were added to the flasks and the volume
of each of the derivatized standards was reduced to about 0.5 ml
by blowing with nitrogen gas. The 0.05-ug/ml standard was made

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up to 1 ml in hexane while the 1.0 and 10.0 ug/ml standards were diluted with hexane to give a final concentration of 0.05 ug/ml. These standards were then quantified by gas-liquid chromatography (GLC).

Clean-up

Florisil (PR 60/100 mesh) was activated at 120C for 24 h and then placed on a roller and at intervals, glass-distilled water added with a syringe until it contained 2% water. The florisil was tumbled overnight to ensure uniform water distribution.

Three grams of the prepared florisil were then packed into a burette between two layers of 2-3 cm of granular anhydrous Na_2SO_4. The column was tapped to ensure even packing of the florisil and 10 ml of 10% diethylether in hexane were passed through it. The eluted solvent was discarded.

After the removal of excess diazomethane, the extract, approximately 1.5 ml, was transferred to the florisil column and eluted with 25 ml of 10% diethylether in hexane. The eluate was collected in a 100-ml round-bottom flask, and flash-evaporated to about 1 ml, then quantitatively transferred to a graduated test-tube. It was then brought up to 2 ml with hexane and analysed on GLC for T, TP, EGBE and MTP.

To determine the recovery from florisil, derivatised analytical standards of T and TP of 0.5 ug/ml with the volume

reduced to about 0.5 ml, were layered on the florisil columns. Elution was done with 25 ml of 10% diethylether in hexane. The eluates were collected in 100-ml round-bottom flasks, reduced to 0.5 ml by flash-evaporation, and then brought up in hexane to a concentration of 0.05 ug/ml and analysed by GLC.

Extracting soil

To 50g of soil sample in a wide-mouth, one-pint Mason® jar was added 80 ml of acetone slightly acidified with H_2SO_4. Thirty grams of anhydrous Na_2SO_4 were added to each sample, which was then blended in a Sorvall Omni mixer at 20V (Varian speed regulator). After blending for 5 min, the solids were allowed to settle and the acetone extract was filtered, under aspiration through a Whatman #1 filter paper in a Buchner funnel, into a conical flask and transferred to a 250-ml measuring cylinder. Extraction was repeated twice with a further 70 ml of acetone on each occasion. The combined extracts were made up to 250 ml in the measuring cylinder. The extraction was similar for sand.

Ten millilitres of the acetone extract, equivalent to 2g of the soil or sand, were transferred to a 250-ml separatory funnel and 50 ml of acidified glass-distilled water (pH 2) were added. Further extraction and clean-up was similar to that as described for water eluates.

Determination of MTP and EGBE vs T and TP

The above procedure of extraction, derivatization and clean-up facilitates the determination of T and TP. Chemically "derivatized TP" = "MTP", therefore to determine MTP and also EGBE, in the samples, aliquots of extracts were cleaned up without derivatizing.

Gas-Liquid Chromatography (GLC) Analysis

A gas chromatograph, Microtek MT-220 equipped with a ^{63}Ni electron capture detector (ECD) was used for the analysis of derivatized T, derivatized TP, and EGBE. The operating conditions are given in Table 2.

T and TP were quantified by comparison with the peak heights of external standards. Standard curves were prepared daily. The analytical reference standards were prepared in hexane.

Untreated samples of soil, sand and their water eluates were extracted and analysed as described; no detectable GLC responses corresponded with those of T, TP, or EGBE.

Analytical reference standards were prepared from T and EGBE of 99.1% purity; and from TP of 99.8% purity. A stock solution of 100 ug/ml in benzene was prepared for derivatization. The final analytical standards of both derivatized T and derivatized TP were 0.05 and 0.02 ug/ml in

TABLE 2

GLC Operating Conditions for the Detection of Derivatized Triclopyr (T), Derivatized 3, 5, 6-trichloro-2-pyridinol (TP), and Ethyleneglycolbutylether Ester of Triclopyr (EGBE).

	T	TP	EGBE
Oven Temp., C	175	175	220
Inlet Temp., C	200	200	230
Detector Temp., C	285	285	285
Retention Time, min	8.43	2.21	8.11
Column, Size:	183 cm x 6.4 mm		
Packing:	4% SE30 ÷ 6% SP2401 on Supelcoport 80/100 Mesh		
Carrier Gas:	Nitrogen, 70 ml/min		

hexane; whereas EGBE was at 0.05 ug/ml.

Recovery studies

Quadruplicate samples of water eluates of untreated soil or sand were fortified with T and TP at 0.001, 0.1 and 1.0 ppm to determine the recovery rates. Similarly, quadruplicate samples of untreated soil or sand were fortified at 0.01, 0.1 and 5.0 ppm. The fortified soils or sand, in Mason® jars, were thoroughly mixed and left in the fume hood for 1 h, to remove the acetone, then allowed to equilibrate at 4C overnight, and extracted the next day.

EGBE was added separately to untreated samples of soil and sand and also to their water eluates. Concentrations were 0.1 and 5.0 ppm for soil and sand; and 0.001, 0.1 and 1.0 ppm for eluates.

Samples of fortified eluates were kept in storage at -20C and subsamples of these were analysed periodically in order to monitor the storage stability of the compounds studied.

IV. RESULTS

Quantification and detection limits

In the GLC analysis, derivatized T and EGBE had single peaks with retention times of 8.43 and 8.11 min respectively. Derivatized TP had two peaks with retention times of 2.21 and 6.14 min respectively. Florisil clean-up, however, removed the second peak and the first peak was used for quantification. Consistent peak heights were obtained with 5-ul injections of 0.05 ug/ml concentrations of T and TP prepared from standards derivatized at 0.05, 1.0 and 10.0 ug/ml. Base on a 6 ul injection with a 10 times dilution of the extracts, the lowest quantification limit for derivatized T, derivatized TP and EGBE were 0.005 ppm. Extract concentrations <0.005 ppm were considered traces and where no responses were recorded by the GLC, the results were "ND" or non-detectable.

Recovery and storage

Recoveries for various levels of T, TP and EGBE in sand, soil and their eluates are shown in Table 3. With the exception of EGBE in soil, no chemical conversion was noted in the various recoveries. About 45.2% of the EGBE fortified in soils were

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TABLE 3

Recovery, in Percent of Added Triclopyr (T), 3,5,6-trichloro-2-pyridinol (TP), and Ethyleneglycolbutylether Ester of Triclopyr (EGBE) from Fortified Sand, Soil, and Eluates, 12 to 18 Hours After Fortification.

Substrate	Forti- fication ppm	Recovery		
		T	TP	EGBE
Sand	5.0	100.8 ± 6.9	95.4 ± 6.0	101.5 ± 4.3
	0.1	92.0 ± 6.8	92.2 ± 5.6	100.3 ± 3.1
	0.01	90.5 ± 7.8	80.3 ± 3.4	not done
Eluates, Sand	1.0	94.7 ± 5.8	90.2 ± 6.7	98.4 ± 3.6
	0.1	90.3 ± 5.8	84.4 ± 3.6	97.0 ± 3.8
	0.001	92.5 ± 3.5	88.1 ± 7.3	91.6 ± 6.6
Soil	5.0	100.0 ± 3.9	94.7 ± 3.3	106.9 ± 4.7 [a]
	0.1	100.0 ± 1.9	98.4 ± 4.0	98.9 ± 5.6 [b]
	0.01	102.0 ± 4.8	80.9 ± 3.0	not done
Eluates, Soil	1.0	104.2 ± 6.6	100.6 ± 7.2	100.8 ± 2.9
	0.1	97.2 ± 2.8	95.6 ± 3.3	96.5 ± 1.4
	0.001	95.8 ± 5.4	80.6 ± 6.1	95.4 ± 3.4

[a] 48.7% as T.   [b] 41.7 % as T.

recovered as T after 12-18 h at 4C, indicating that hydrolysis had occurred overnight.

Periodic analysis of aliquots of eluates, soil and sand stored at -20C, for T, TP, MTP and EGBE gave similar results consistently indicating that there was no detectable chemical change in storage over 8 months at -20C.

Moisture, pH and composition of soil

The natural pH of the soil and sand and of their eluates are shown in Table 4. The distilled water used to simulate rain for leaching the columns had a pH of 5.5 . Moisture content determinations prior to leaching showed 50.8 ± 2.0 % in soil and 2.9 ± 0.7 % in sand. After leaching, their moisture contents were higher (Table 5); especially in the lower sections.

The soil contained 34% organic matter. The particle size distribution was: 45.4% sand, 46.3% silt and 8.3% clay. The soil as such had a loamy texture.

Leaching, Sand.

The concentrations of T found in each eluate of the duplicated sand columns, treated with technical T, did not differ significantly (Chi-square test, $P<0.05$). This was also noted for the duplicated columns treated with EGBE. The means of the concentrations of T leached in the eluates of both the sand

TABLE 4

pH of Soil, Sand, and Respective Eluates.

Substrate	pH
Soil [a]	3.4
Soil Eluates [b]	3.45 to 3.90
Sand [a]	7.0
Sand Eluates [b]	6.4 to 7.0

[a] Prior to leaching.   [b] Range of pH of 27 eluates.

TABLE 5

Moisture Contents of Soil and Sand Core Sections after Leaching.   Means and Standard Deviations (n = 4).

Section Number	Moisture Contents, %	
	Soil	Sand
1	61.6 ± 1.8	2.8 ± 0.5
2	62.3 ± 1.0	3.6 ± 0.9
3	64.8 ± 1.0	4.6 ± 0.5
4	66.9 ± 1.9	9.9 ± 0.8

column treatments are as shown in Figures 3 and 4.

Low levels (<0.01 ppm) of T were detected in the first eluate, collected after the equivalents of 2.54 cm (1 in) of rain had passed through the technical T and EGBE treated sand columns. Thereafter, they increased to a maximum of 2.95 and 3.58 ppm respectively, after about 10 cm (4 in) of rainfall. For the sand columns treated with technical T, a rapid decline followed until about 18 cm or 7 in of rainfall had moved through the columns (Figure 3). Then, the decline tapered gradually.

For the sand columns treated with EGBE, the decline was gradual to about 0.5 ppm after about 33 cm or 13 in of rainfall had passed through, and then tapered to <0.1 ppm at 46 cm, or 18 in of rainfall (Figure 4). Leaching patterns of triclopyr and EGBE were highly correlated (r=0.836).

Traces (<0.005 ppm) of TP were detected in some of the eluates from both the columns treated with technical T and EGBE. Similarly, traces (<0.005 ppm) of EGBE were detected in several of the eluates from the sand columns treated with EGBE.

The total quantities of T, expressed as % of amount applied, leached out of sand columns treated with technical T and EGBE are as shown in Figure 5. Recovery, in the form of T, was complete 34 days after treatment of sand with EGBE, whereas, for T-treated sand, 65% were found in the eluates after 54 days of leaching.

Analysis of the individual sections of the sand columns, showed that T was present in the columns treated with technical

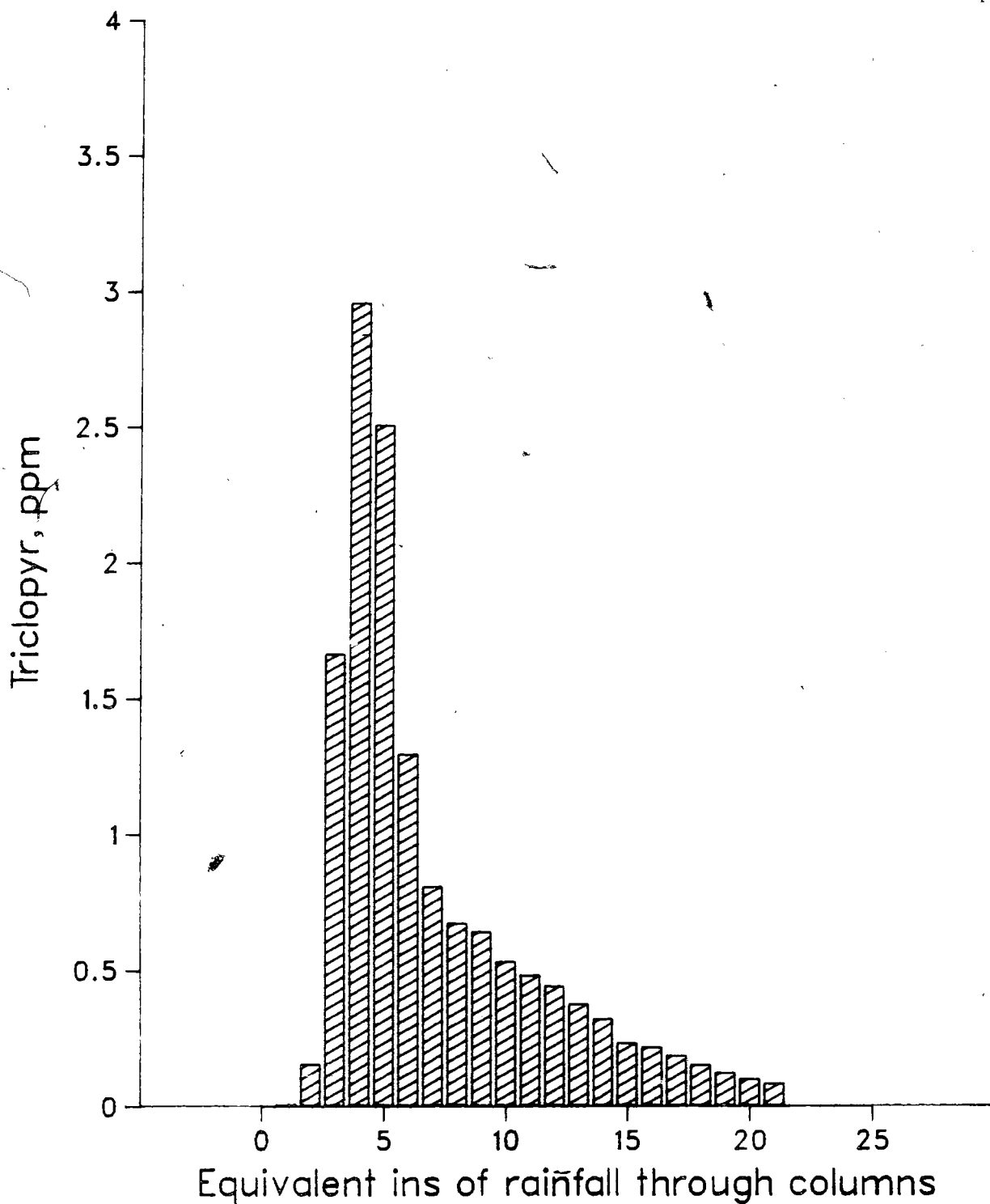Figure 3. Concentrations of Triclopyr in Water Eluates of Sand Columns Treated with Technical Triclopyr.

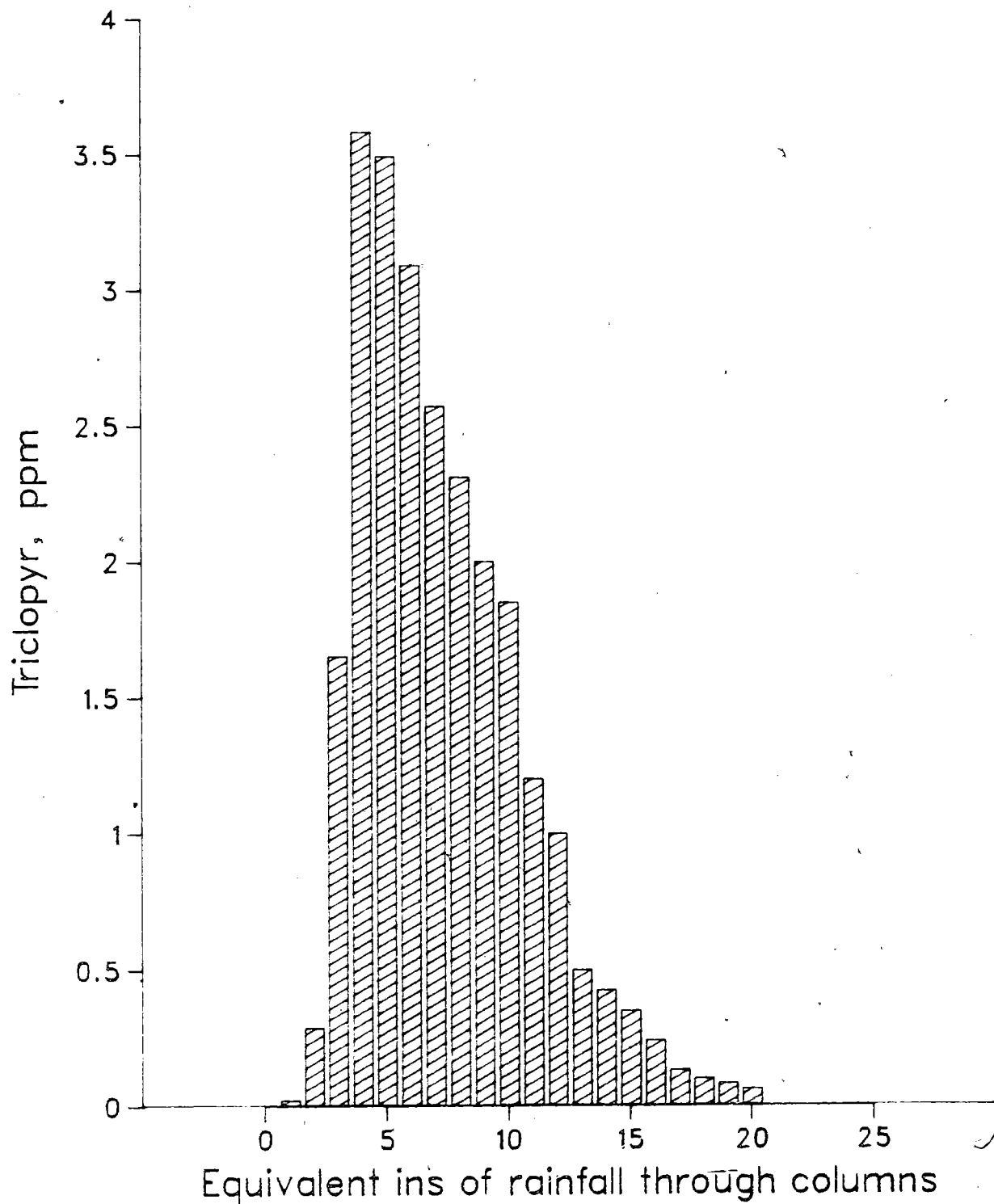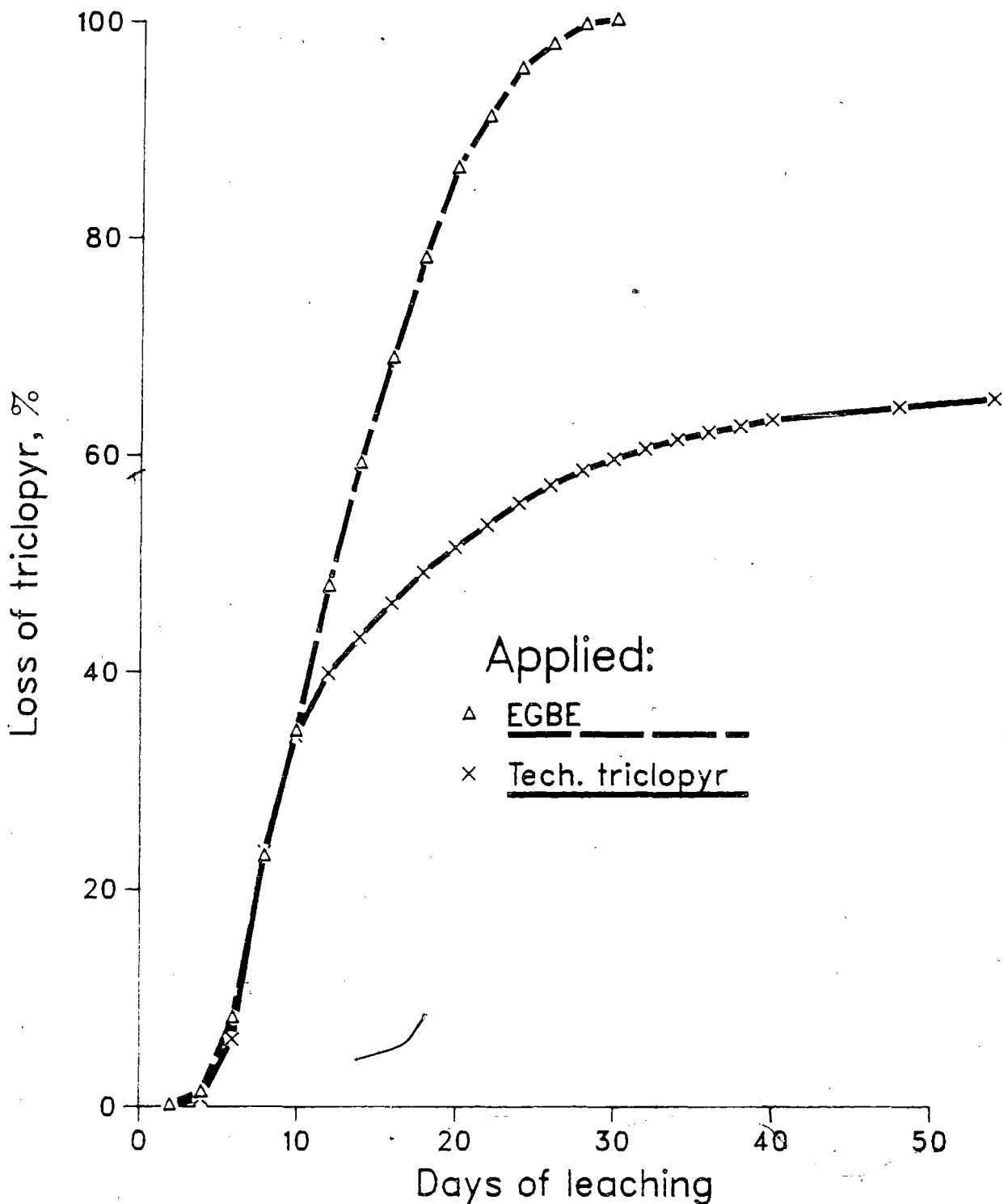Figure 4. Concentrations of Triclopyr in Water Eluates of Sand Columns Treated with EGBE.

Figure 5. Loss of Triclopyr From Sand Columns, in % of Triclopyr Applied to the Top of Each Column.

T, but not in those treated with EGBE (Table 6). The concentrations of T were low, although higher concentrations were found in Sections 1 and 4 than in Sections 2 and 3. Neither TP, EGBE nor MTP were detected. The amount of T recovered from these columns was 9.75% of that applied originally (Table 7). Thus, total amounts of T recovered in the eluates and sand from these columns were approximately 75% of that applied (Fig. 5 and Table 7).

Leaching, Soil.

No residues were found in eluates nor in sections 2,3,4 of any of the soil columns, regardless of treatment (Table 6). Analyses showed the presence of T, TP and MTP only in Section 1 of each soil column. The concentrations of TP were >10 times those of MTP or T, namely [TP] >>>> [MTP] > [T] (table 6). The quantities of TP, as such, were more than one order of magnitude above that of T or MTP (Table 7). The differences between TP and T or MTP were statistically significant (P>0.05) but not between T and MTP (P <0.05). The quantities of herbicide and its residues found in soils treated with technical T were not statistically different (P<0.05) from those found in soils treated with EGBE.

TABLE 6

Concentrations (ppm, means of two columns) of Triclopyr (T), 3, 5, 6-tri-chloro-2-pyridinol (TP), and 2-methoxy-TP (MTP) in the Sections of the Soil or Sand Columns, Found by Analysis After the Leaching Had Been Terminated.

Column	Treat-ment [a]	Core Section	ppm		
			T	TP	MTP
Sand	T	1	0.296	0[b]	0
		2	0.012	0	0
		3	0.005	0	0
		4	0.032	0	0
	EGBE	1	0	0	0
		2	0	0	0
		3	0	0	0
		4	0	0	0
Soil	T	1	0.158	1.935	0.402
		2	0	0	0
		3	0	0	0
		4	0	0	0
	EGBE	1	.214	2.667	0.206
		2	0	0	0
		3	0	0	0
		4	0	0	0

[a] see Table 1.   [b] Not Detectable.

TABLE 7

Amounts (ug, means of two columns) of Triclopyr (T), 3,5,6-trichloro-2-pyridinol (TP), and 2-methoxy-TP (MTP) Recovered from Soil or Sand After Completion of Leaching. EGBE was Not Detected.

Treatment [a/]	T	TP [b/]	MTP [b/]	Total	% of Applied
		S O I L			
T	81.5	1,666	304.8	2,052	58.6
EGBE	123.2	1,998	144.2	2,266	64.7
		S A N D			
T	341.3	0.[c/]	0	341.3	9.75
EGBE	0	0	0	0	—

[a/] see Table 1.   [b/] as Triclopyr equivalent.   [c/] Not Detectable.

V. DISCUSSION

Treatment of the top layers of the soil and sand columns with technical T or EGBE at 3.5 mg of the active ingredient per column is equivalent to 5.6 kg/ha (5 lbs/acre). It approximates the mean of the range of triclopyr rates (0.28 to 11.2 kg/ha) reported. It exceeds the rates reported effective for conifer release and the control of general broad-leaved weeds, which range from 1 to 2 lbs/acre (Byrd et al., 1975). Assuming the latter were to be adopted for use in British Columbia, an interpretation of my results can be expected to be conservative, i. e., to be in the interests of environmental protection and with a bias towards caution.

The translocation of triclopyr in sand with water is shown in Figures 3 to 5 and Tables 6 & 7. With the equivalent of 17 in. of precipitation, one inch applied every second day, all residues leached through sand which had been treated with EGBE. Leaching through sand treated with technical T, however, was incomplete, even after the equivalent of 27 in. of rain had been passed through these columns during a 54-day period. Approximately 10% of the applied T were still in the sand and about 25% could not be detected as T, TP, or MTP, probably because of chemical break-down to innocuous molecular species. The faster movement of residues through sand treated with EGBE was probably caused by surfactants in the formulation.

Considering that the acute toxicity to aquatic organisms of EGBE is much higher than that of T, it is most significant to note that only T, and no quantifiable EGBE was detected (only traces, i. e., <0.005 ppm were detectable in a few samples from EGBE-treated sand). The highest concentration of T in two of the eluates was near 3.5 ppm (Fig. 4). Although such a concentration of EGBE is lethal to fish (Weed Sci. Soc. Am., 1983), LC_{50}s of T are 25 to 50 times higher than 3.5 ppm, and concentrations of T, lethal to daphnia, are 100 to 600 times higher (Gersich et al., 1984).

The results have shown that the sand had low - if any - sorptive capacity for the herbicide, supporting the multitude of reports in the literature ascribing sorption of pesticide residues in soils to their organic matter and clay contents. It is doubtful that pure sand, devoid of any clay and/or organic matter and thus of sorptive capacity, will sustain growth of trees to make a forest. As a corollary, it should be doubtful, that a deposit of pure sand will be sprayed with triclopyr. But even if this were so, these results do not support prediction of disaster. They suggest, instead, that leaching from sand into natural waters, providing it occurred at all, would present little or no hazard. Although EGBE, unlike T, is acutely toxic to fish at 0.74 to 0.87 ppm (Weed Sci. Soc. Am., 1983), it would not get into fish-bearing waters because of hydrolysis to T prior to reaching such aquatic biota. Rapid dilution of T-containing eluates upon entering natural water bodies would

reduce the likelihood of adverse effects on aquatic life even further.

No T, TP, EGBE or MTP were detected in the soil eluates (Tables 6, 7), indicating that no residues leached through the selected forest soil with water equivalent to a total of 27 in. of rainfall. Furthermore, there was no movement even within the soil profile (Table 6), suggesting a high affinity and sorptive capacity of this soil for T and its congeners. Even if higher rates were to be applied, leaching through this soil should not be expected. The organic matter content of 34% probably contributed mostly to this, for Hamaker and Goring (1976) noted the sorptive capacity of soils for T increased with higher organic matter content.

T was degraded in the soil to a large extent; only low concentrations were found after 54 days, namely 2.3% of technical T applied originally, or 4% of the total recovered by analysis (Table 7). The soil's low pH (Table 4) may have promoted the degradation of T, because only T was found in the sand (Table 7) and its eluates. The major metabolite in the soil was TP, accounting for 81% of the recovered residues, while MTP was 15%.

The residues in the soils treated with EGBE were T, TP, and MTP, respectively with 5.5, 88, and 6.5 % of the total, i. e., TP was the major breakdown product in EGBE-treated soils also. The larger amount of TP and smaller amount of MTP, than in the soils treated with T, suggested a sequence of reactions as shown

in Figure 6: TP is formed from T (Fig. 6, II), a reaction which must be anteceded by hydrolysis of EGBE with a concomitant build-up of T, and which does not occur in soils treated with T; in the latter, maximal concentrations of T are provided with the treatment. But in EGBE-treated soils, no T is present at the outset; it must be formed by hydrolysis of EGBE before further reactions with T as the substrate can take place. Reaction I in the sequence (Fig. 6, I) delays the build-up of MTP in EGBE-treated soils. Conversely, in T-treated soils Reaction I does not take place and MTP accumulation is not delayed accordingly. With the exception of EGBE on sand, the overall recovery of residues was 75% or less, indicating that the degradation of T was not only to TP and MTP but also to other innocuous compounds. The first degradation product of EGBE in sand is T; all of the EGBE applied to sand was recovered as T.

EGBE (Fig. 6) has two types of bonds, an ester bond at Site A and an ether bond at Site B, which yield upon hydrolysis T and TP, respectively. The results indicated that the ester bond was more susceptible to hydrolysis than the ether bond. The rapid hydrolysis of the ester was supported also by soil samples fortified with EGBE for recovery studies: when held at 4C for 12-18 h after fortification (Table 3), nearly 50% of the EGBE were hydrolyzed and recovered as T. In view of these results, it is suggested that the dynamics of the formation of TP and MTP with time be investigated.
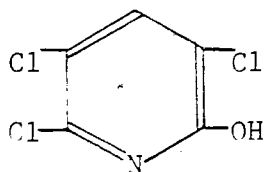
Site A

Site B
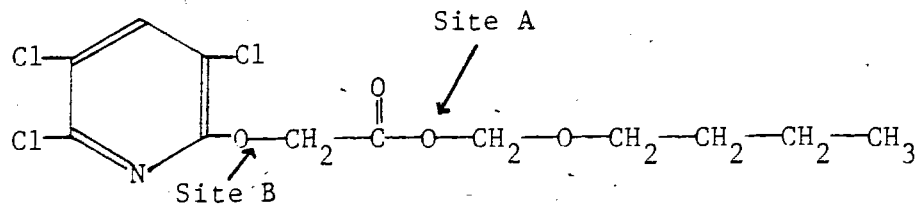
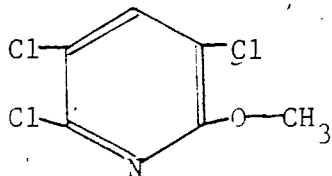Ethyleneglycolbutylether ester (EGBE) of Triclopyr

I (Hydrolysis)
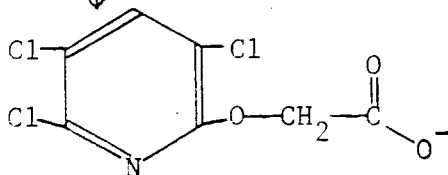
Triclopyr (T)

II (Hydrolysis)

3,5,6-trichloro-2-pyridinol (TP)

III (Methylation)

2-methoxy-3,5,6-trichloropyridine (MTP)

Figure 6. A Possible Pathway of Reactions of Ethyleneglycol-
butylether Ester of Triclopyr in the Soil.

TP appears to be formed quite rapidly from T, followed by much slower rates of methylation to MTP, which may be chemically more stable, than T and TP, and thus continue to accummulate whereas concentrations of TP may have peaked earlier than 54 days after treatment and will no longer be replenished from the pool of largely depleted T (Table 7). The great quantities of TP found in the soil indicated the likelihood that it was predominantly formed from T, as proposed in Fig. 6.

Probable involvement of microorganisms in the degradation of EGBE and T is indicated by the properties of the soil tested and reports of greater density of microorganisms near colloidal surfaces, where most pesticides are bound, than in solution (Burns, 1978). Metabolism of T in the soil has been suggested by Brown and Bos (1977) when they found that the half-life of T at 25C under aerobic conditions was 8-18 days and under anaerobic conditions was 42-130 days. The methylation of TP to MTP in the soil is probably mediated by microorganisms, a mechanism proposed by Roberts and Marshall (1978). The amounts of MTP present (Table 7) appeared to indicate its slow formation via TP. Such formation in the soil, could occur immediately with technical T, whereas T was only made available following break-down of EGBE. Based on these results, a pathway of reactions has been proposed (Fig. 6).

Hamaker and Goring (1976) showed that T was less persistent in silty clay loam of pH 5.8 and 4.2% organic matter content, than in loam of pH 6.5 and 0.8% organic matter content. The

amounts of T, the active ingredient that persisted in the sand columns treated with technical T, were equivalent to field application rates of 0.56 kg/ha, whereas in the soil columns fortified with technical T and EGBE, they were 0.11 and 0.2 kg/ha respectively. These levels were below those tolerated by sitka spruce, hemlock and some pine species (McCavish, 1980), and thus would be unlikely to cause phytotoxicity. T bound to organic matter ("bound residues", Hamaker and Goring, 1976), quite likely reduces such hazards even further.

In summary, no movement of the herbicides was found to occur in the cedar-hemlock forest soil studied. The probability is high that T and EGBE will neither persist nor move vertically with water in soils of B. C. coastal forests and that leaching through such soils into sub-surface water, with subsequent transport into fish-bearing aquatic environs, is unlikely to pose a hazard in the field if the herbicide is used. By contrast, the movement of triclopyr in sand, devoid of organic matter and clay, makes it advisable to investigate these relations in soils with sorptive characteristics approaching those of pure sand, although contamination of waters with EGBE would not be indicated.

REFERENCES

Anonymous 1982. (Unpublished) A trial-cum-demonstration on the use of Garlon® 250 in oil palm plantations. 8pp. Research and Development Report, Dow Chemical Pacific Ltd., Kuala Lumpur, Malaysia.

Bailey, G.W. and White, J.L. 1970. Factors influencing the adsorption, desorption and movement of pesticides in soil. Res. Rev. 32 :29-92.

Bovey, R.W., Hein, H.Jr. and Meyer, R.E. 1984. Effect of herbicides on the production of common buffelgrass (Cenchrus ciliaris). Weed Sci. 32(1) :8-12.

Bovey, R.W., Ketchersid, M.L. and Merkle, M.G. 1979. Distribution of triclopyr and picloram in huisache (Acacia farnesiana). Weed Sci. 27(5) :527-531.

Bristol, R.W. 1981. Control of sweet brier using picloram, triclopyr and 2,4,5-T applied with modified drench gun. Proc. N.Z. Weed and Pest Control Conf. 34 :144-147.

Brown, J.G. and Bos, G. 1977. Triclopyr, a new herbicide for control of woody plants. Proc. EWRS Symp. on Methods of Weed Control and their Integr., p121-128. 1977.

Burns, R.G. 1978. Enzyme activity in soil : some theoretical and practical considerations. In : Soil Enzymes (R.G. Burns Eds.) p295-340. Academic Press, London and New York.

Byrd, B.C. and Colby, R.W. 1978. Woody plant control with low volume applications of Garlon® 3A herbicide. Down to Earth 34(2) :7-11.

Byrd, B.C., Wright, W.G. and Warren, L.E. 1975. Vegetation control with Dowco® 233 herbicide. Down to Earth 30(4) :8-12.

_____. 1974. Vegetation control with 3,5,6-trichloropyridyloxyacetic acid. (Abstract). Proc. North Central Weed Control Conf. 29 :137-138.

D'Anjou, B. 1985. Garlon® 4E herbicide trial at McGuire Creek. Pest Management Progress 4(1) :25-26.

Fears, R.D. and Dickens, R. 1978. Aerial application of triclopyr for brush control. Down to Earth 34(3) :11-15.

Forgie, C.D., Lobb, P.G. and Dryden, P.J. 1981. A comparison of a picloram/triclopyr mixture with other herbicides for

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blackberry control. <u>Proc. N.Z. Weed and Pest Control Conf.</u> <u>34</u> :148-151.

Forgie, C.D., Saunders, D.G. and MacDiarmid, B.N. 1977. Blackberry control with triclopyr. <u>Proc. N.Z. Weed and Pest Control Conf.</u> <u>30</u> :71-75.

Foy, C.L. and Chang, I.K. 1979. Studies on the mode of action of some alpha-substituted pyridine compounds in plants. <u>Adv. in Pesticide Sci.</u> <u>79</u> :499-503.

Gersich, F.M., Mendoza, C.G., Hopkins, D.L. and Bodner, K.M. 1984. Acute and chronic toxicity of triclopyr triethylamine salt to <u>Daphnia magna</u> Straus. <u>Bull. Environm. Contam. Toxicol.</u> <u>32</u> :497-502.

Gorrell, R.M., Bingham, S.W. and Foy, C.L. 1981. Control of Horsenettle (<u>Solanum carolinense</u>) fleshy roots in pastures. <u>Weed Sci.</u> <u>29(5)</u> :586-589.

Gratkowski, H.J. 1978. Herbicides for shrub and weed tree control in Western Oregon. General Technical Report PNW-77, 48pp. Forest Service, USDA Portland, Oregon.

Gratkowski, H.J., Stewart, R.E. and Weatherly, H.G. 1978. Triclopyr and Krenite herbicides show promise for use in Pacific Northwest Forests. <u>Down to Earth</u> <u>34(3)</u> :28-31.

Green, G.W. 1984. Garlon (Triclopyr): A case history of significant obstacles to its registration and use in forestry in Canada. p94-101 <u>In</u> Proc. of Seminar on herbicides and forest renewal, Ottawa, Nov. 15, 1984.

Haagsma, T. 1975. Dowco® 233 herbicide - a possible new tool in vegetation management. <u>Down to Earth</u> <u>30(4)</u> :22-24.

Hamaker, J.W. and Goring, C.A. 1976. Turnover of pesticide residues in soil. <u>In</u>: Bound and Conjugated Pesticide Residues (D.D. Kaufman, G.G. Still, G.D. Paulson and S.K. Bandal eds.) p219-243, ACS Symp. series 29, Washington, D.C.

Haywood, J.D. 1980. Preparing pine planting sites with picloram pellets. <u>Proc. Southern Weed Sci. Soc.</u> <u>33</u> :115-118.

Hogue, E.J., Khan, S.U. and Gaunce, A.P. 1981. Leaching of four orchard herbicides in soil columns. <u>Can. J. Soil Sci.</u> <u>61</u> :401-407.

Howard, S.W., Dirar, A.E., Evans, J.O. and Provenza, F.D. 1983. The use of herbicides and/or fire to control Saltcedar (<u>Tamarix</u>). <u>Proc. of Western Soc. for Weed Sci.</u> <u>36</u> :65-72.

Jacoby, P.W. and Meadors, C.H. 1983. Triclopyr for control of Honey Mesquite (*Prosopis juliflora* var. *glandulosa*). Weed Sci. 31(5) :681-685.

Ketchersid, M.L. and Merkle, M.G. 1978. Dissipation of VEL 4207 from Texas soil. Proc. Southern Weed Sci. Soc. 31 :271-277.

Khan, S.U. 1980. Pesticides in the soil environment. Elsevier Scientific Publishing Co. Netherlands. 240pp.

Khan, S.U. 1974. Adsorption of 2,4-D from aqueous solution by Fulvic acid-clay complex. Environ. Sci. Technol. 8 :236-238.

King, M.G. and Radosevich, S.R. 1979a. Absorption of two herbicides by Tanoak. Proc. of Calif. Weed Conf. 31 :39-42.

_____. 1979b. Tanoak (*Lithocarpus densiflorus*) leaf surface characteristics and absorption of triclopyr. Weed Sci. 27(6) :599-603.

Klingman, G.C., Ashton, F.M. and Noordhoff, L.J. 1982. Weed Science : Principles and practices. John Wiley and Sons publ. New York. 449pp.

Lauterbach, P. and Warren, L.E. 1982. Control of resprouting hardwood clumps with applications of triclopyr ester by hovering helicopter. Proc. of Western Soc. of Weed Sci. 35 :36-38.

Lee, S.A., Fadzerum Ahmad and Lee, H.K. 1984. White flower weed (In Malaysian Language). Berita Penyelidikan Mardi 13 :13-14.

Lichy, C.T. 1978. Brush control with Garlon® herbicides alone and in combination with Tordon® 101 mixture or 2,4-D herbicides using three methods of application. Down to Earth 35 :20-24.

Lim, T.M. and Abdul Aziz Syed Abdul Kadir. 1981. Triclopyr, a new arboricide for rubber. Proc. Planters Conf. (RRIM), p327-336, 1982.

Luttmerding, H.A. 1980. Soils of the Langley-Vancouver Map Area. Report No. 15, British Columbia Soil Survey, Div. of Planning and Assessment, Min. of Environ., B.C. 1980.

MacDiarmid, B.N. 1977. Properties and activity of triclopyr on some New Zealand brushweeds. Proc. N.Z. Weed and Pest Control Conf. 30 :66-70.

Mann, R.K., Rosser, S.W. and Witt, W.W. 1983. Biology and control of tall ironweed (*Vernonia altissima*). Weed Sci.

31(3) :324-328.

Maybury, R.B. 1980. Laboratory manual for pesticide residue analysis in agricultural products. Laboratory Services Div., Food Production and Inspection Branch, Agriculture Canada, Ottawa, Ontario.

McCavish, W.J. 1980. Herbicides for woody weed control by foliar application. Proc. British Crop Protection Conf. - Weeds. p729-737.

McKellar, R.L., Schubert, O.E., Byrd, B.C., Stevens, L.P. and Norton, E.J. 1982. Aerial application of Garlon® 3A herbicide to a West Virginia watershed. Down to Earth 38(2) :15-19.

Moseman, T.E. and Merkle, M.G. 1977. Analysis, persistence and activity of triclopyr. Proc. Southern Weed Sci. Soc. 30 :64.

Radosevich, S.R., Passof, P.C. and Leonard, O.A. 1976. Douglas fir release from Tanoak and Pacific madrone competition. Weed Sci. 24(1) :144-145.

Radosevich, S.R. and Bayer, D.E. 1979. Effect of temperature and photoperiod on triclopyr, picloram and 2,4,5-T translocation. Weed Sci. 27(1) :22-27.

Reynolds, P.E., Hendler, R.J., Betsch, W.D. and Ollice, W. 1983a. Triclopyr amine control of large trees on a West Virginia pipeline row. Proc. of Northeastern Weed Sci. Soc. 37 :279-285.

_____. 1983b. Preliminary evaluation of triclopyr ester efficacy on a West Virginia pipeline row. Proc. of Northeastern Weed Sci. Soc. 37 : 286-290.

_____. 1983c. Evaluation of aerial dormant spraying with triclopyr ester on a West Virginia pipeline row. Proc. Northeastern Weed Sci. Soc. 37 :291-296.

Roberts, J.R. and Marshall, W.K. 1978. Ecotoxicology of chlorpyrifos. National Res. Council of Canada Publ. No. 16079.

Rolston, M.P. and Devantier, B.P. 1983. Alternative herbicides to 2,4,5-T for gorse control. N.Z. J. of Experimental Agric. 11 :91-94.

Saka, H. 1983. Current trends in foliage-applied herbicides. Japan Pesticide Information No. 42 :28-35.

Siltanen, H., Rosenberg, C., Raatikainen, M. and Raatikainen, T.

`1981. Triclopyr, glyphosate and phenoxyherbicide residues in cowberries, bilberries and lichen. **Bull. Environm. Contam. Toxicol.** 27 :731-737.

Spencer, E.Y. 1982. Triclopyr. **In** : Guide to chemicals used in crop protection. Res. Branch Agric. Canada Publ. 1093.

Stevenson, F.J. 1976. Organic matter reactions involving pesticides in soil. **In** : Bound and Conjugated Pesticide Residues (D.D. Kaufman, G.G. Still, G.D. Paulson and S.K. Bandal, eds.)p180-207, ACS Symp. series 29, Washington. D.C.

Teoh, C.H., Toh, P.Y. and Khairudin, H. 1982. Chemical control of _Asystasia_ _intrusa_ (Bl.), _Clidemia_ _hirta_ (Don.) and _Elettariopsis_ _curtisii_ (Bak.) in rubber and oil palm plantations. Int. Conf. on Plant Protection in the Tropics, 1-4 March, 1982, Kuala Lumpur, Malaysia. Preprint X-1 14pp.

Torstensson, L. and Stark, J. 1982. Persistence of triclopyr in forest soils. **In : Weeds and Weed Control, 23rd Swedish Weed Conf., Uppsala, 1982** :393-399.

Voeller, J.E., Smith, L.L. and Holt, H.A. 1976. Right-of-way high volume applications of triclopyr (Dowco® 233). **Proc. Southern Weed Sci. Soc.** 29 :334-336.

Walker, A. and Crawford, D.V. 1968. The role of organic matter in adsorption of the triazine herbicides by soils. **In** : Isotopes and Radiation in soil organic matter studies. **Proc. 2nd Symp. Int. Atomic Agency** (Vienna), p91-108.

Weed Sci. Soc. of America. 1983. Triclopyr. **In:** Herbicide handbook p467-470. 5th edition. Weed Sci. Soc. of America. Champaign, Ill. 1983.

Wershaw, R.L., Burcar, P.J. and Goldberg, M.C. 1969. Interaction of pesticides with natural organic material. **Environ. Sci. Technol.** 3 :271-273.

Wilson, D.M. 1973. Studies on the residual properties of high-purity chlordane (Velsicol HCS-3260) in soils and crops. M. Sc. Thesis, Simon Frase University, Burnaby, B.C. Canada.