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# Residual Characteristics of Picloram In Grassland Ecosystems

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	Contents
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	erenness of culturated territoristic field user a second state of the
	Summary
	Introduction
	Toxicity of Picloram
	Methods of Residue Detection
	Picloram Residues and Susceptible Crops
	Photolytic Degradation of Picloram
	Vegetational Areas of Texas Studied
	Theoretical Routes of Dissipation of Picloram from Rangeland
	Dissipation from Soils
	Role of Temperature
	Influence of Soil Properties
	Movement and Loss of Picloram Through Soil Profiles
	Subhumid Rangeland Sites
	Vegetated Areas
	Fallowed Areas
	Tropical Sites
	Vegetated Areas
	Fallowed Areas
	Semiarid Sites
	Influence of Slope on Distribution of Picloram in Soil Profiles
	Persistence of Picloram in Soils
	Influence of Formulation of Residual Properties of Picloram in Soil
	Movement of Picloram in Surface Water
	Dissipation of Picloram from Impounded Water Sources
	Dissipation of Picloram from Grasses
	Subhumid Areas
	Semiarid Areas
	Dissipation of Picloram from Broadleaf Herbs
	Dissipation of Picloram from Woody Species
	Subhumid Areas
	Tropical Areas
	Semiarid Areas
and a start of the st	Acknowledgment
	Literature Cited

### Summary-

Picloram, applied alone or in combination with 2,4,5-T, has potential for control of many species of herbaceous weeds and woody plants on grasslands. Picloram is relatively persistent, and complex factors influence the rate of dissipation from various segments of the ecosystem. Its persistent nature is one quality responsible for its effectiveness as an herbicide. Little data are available concerning the mode or degree of loss of picloram from the time it leaves the spray boom until it reaches the target areas. However, once picloram reaches plant and soil surfaces, there is progressive decline within the ecosystem. It is susceptible to photodecomposition. Picloram is mobile within the ecosystem and follows the movement of water.

Theoretically, picloram reaching the soil surface, if not photodecomposed, may move vertically through the profile, laterally on the soil surface and to a limited degree laterally through the profile. The degree, direction and rate of movement are dictated by explicit characteristics of the vegetation and soil and the rate of picloram applied. In general, when a low rate (0.5 pound per acre or less) is applied to rangeland, especially those with heavy-textured soils, downward movement is much less than where higher rates are applied to highly permeable, sandy soils. In fine sandy soils, detectable residues were rarely moved beyond the top foot of the profile following the application of only 0.25 pounds per acre to rangeland in North and West Texas. Present data from various sources do not indicate extensive sorption of picloram by the soil colloid or rapid detoxification by microorganisms. Dilution in the soil may be one of the most important, practical means of dissipating picloram. Subsurface lateral movement is also dependent on direction and rate of soil water flow. Subsurface lateral movement, however, is apparently of lesser importance than vertical mobility in the soil profile. On slopes exceeding 3 to 4 percent, lateral subsurface movement may be more important than indicated by available data especially following high application rates and heavy rainfall.

Movement over the soil surface is governed primarily by intensity of rainfall, time-lapse from application to the first rain, rate of picloram applied, density and botanical composition of vegetation cover, texture of soil, and slope of the land. The longer the exposure on the soil surface before rainfall, the less picloram is available for movement. Rainfall of low intensity, especially before heavy rainfall, lessens the chance of surface runoff due to penetration of the soil by picloram. In NorthTexas, 17 parts per billion (ppb) of picloram occurred in surface runoff after application of 0.25 pound per acre to highly permeable, sparsely vegetated soils. Water samples were collected 10 days after treatment, immediately after applying 4 inches of simulated rainfall over a 9-hour period. Applications of 1 and 2 pounds per acre of picloram to rangeland in South and Southwest Texas did not result in detectable residues in domestic water wells where samples were taken for up to 2 years following application.

Once runoff water was moved to surface watering ponds under experimental conditions, dilution of picloram residues in the ponds prevented detection. Current methods allow detection of one part picloram per billion parts of water. Direct application of picloram, under experimental Pictorani, tapplied atome or in combination with 2,4,5-T, has potential or control of many speciesoft hopharisons werets and woody plants on grads and. Pictoran is relatively presisters, and complex factors (affuence the are of dissipation from various segments of the convision. Its permetern to the instruction from various segments of the convision. Its permetern that are available concerning the mode or degree of loss of pictoran from the firm Theorem to provide the interview as an herbicide. Little are from Theorem to the specify boom until it reaches the target areas. How the firm Theorem reactive plants first will be reaches the target areas. How the firm within the consistent first boom until it reaches the marget areas. How believes first within the second state of the superprisition.

conditions, equivalent to 1 or 2 pounds per acre showed that dilution was an important mode of picloram dissipation. Dissipation curves, concentration of picloram in pond water versus time, indicate loss to be concentration dependent. Initial loss rates are rapid, then concentrations "level off" at 1 or 2 ppb. However, these low concentrations may be detectable at up to a year after treatment of ponds. Research indicates vegetative growth of sensitive field crops would probably not be reduced using a single irrigation of water containing 1 to 4 ppb of picloram. Large volumes of water containing 4 ppb of picloram repeatedly applied to seedlings would probably reduce crop growth. However, residues of 10 ppb or more in irrigation water could severely affect the growth of some sensitive crop seedlings.

Recent research in dry areas of Texas indicate rapid initial loss of picloram from grasses. Loss rates of 2.5 to 3 percent per day for 30 days were measured. There are indications, however, that grass roots may extract picloram from the soil profile and transport it to aerial portions of the plants. Such accumulations have not been observed in more humid areas of the state where rates of four to eight times those used in drier areas were applied and the picloram was rapidly leached to the lower portions of the soil profile.

Picloram residues in the environment do not appear harmful to mammals, fish, birds or insects which inhabit the ecosystem. Mammals are tolerant to relatively high concentrations of the herbicide without displaying detrimental affects. Picloram passes rapidly, intact, through mammalian systems. Biological significance is related primarily to susceptible plant life, especially cultivated food and fiber crops, growing adjacent to rangeland. Damage to cotton and vegetable crops in adjoining areas is of the greatest concern to rangeland managers when chlorophenoxy herbicides are applied because of possibilities of drift. Similar or more extensive crop injury could result from picloram if drift were allowed. However, for many weed species, picloram may be applied in the fall when susceptible crops are not grown. Pelleted and granular formulations of picloram would minimize the drift hazard.

4

# Residual Characteristics of Picloram In Grassland Ecosystems

R. W. Bovey and C. J. Scifres\*

(INCE ITS INTRODUCTION (34) AS A GROWTH REGULATOR, J 4-amino-3,5,6-trichloropicolinic acid (picloram) has demonstrated phytotoxicity over prolonged periods and has been widely evaluated for control of herbaceous weeds and woody plants in grasslands. An estimated 88 of the 107 million acres of Texas grasslands are infested with woody plants that reduce total lorage production (62). Only about 2 percent, or 1.7 million acres, of these grasslands were treated in 1969 for brush control.<sup>1</sup> About 0.98 million acres were treated with herbicides; the remainder were deared of woody plants by mechanical methods. The potential for treatment of extensive acreages with economical herbicides exists. However, the chemicals must be phytotoxic to a broad spectrum of undesirable species yet safe for use near desirable plants and animals.

Chlorophenoxy herbicides such as (2,4–dichlorophenoxy)acetic acid (2,4–D) and (2,4-5–trichlorophenoxy)acetic acid (2,4,5–T) are widely used for pasture and rangeland improvement. In recent years, picloram has been studied extensively by research and extension personnel. Consequently, a wealth of information concerning the proper use and potential hazards of picloram has been accumulated.

The susceptibility of some problem woody species in Texas to 2,4,5–T, picloram, and picloram combined with 2,4,5–T is shown in Table 1. Many species, tolerant of economical rates of 2,4,5–T and related chlorophenoxyacetic acid herbicides, can be controlled by sprays of picloram or mixtures of picloram with 2,4,5–T. The effectiveness of a 1:1 ratio of picloram + 2,4,5–T for control of honey mesquite *Prosopis juliflora* (Swartz) DC. var. *glandulosa* (Torr.) Cockrell) in semiarid areas (54) and for control of other species in sub-humid regions (9) has been established. Piclo-

Personal communication, Garlyn Hoffman, Extension range brush and weed control specialist, Texas A&M University, College Station.

The information given herein is for research purposes only. Reference to commercial products or trade names is made with the understanding that no discrimination is intended and no endorsement by Texas A&M University, The Texas Agricultural Experiment Station or U.S. Department of Agriculture is implied. ram alone, applied in the spring or fall, effectively controlled huisache (Acacia farnesiana (L.) Willd.) (15). A portion of the picloram could be replaced with 2,4,5–T and huisache control maintained if 1 pound per acre of each herbicide was applied. Picloram, applied to the soil in granular or pelleted form, controlled some species such as lotebush (Condalia spp.) and agarito (Berberis greggii A. Gray) that are not controlled by foliar sprays (Table 1). However, honey mesquite can be controlled by foliar sprays only. Some species such as Texas persimmon (Diospyros texana Scheele) and lime prickly ash (Zanthoxylum fagara (L.) Sarg.) are not effectively controlled by 2,4,5-T or picloram.

Most woody species susceptible to 2,4,5–T are more effectively controlled in the spring at specific growth stages than in the fall. Most species are also most susceptible to picloram at the growth stage of maximum susceptibility to 2,4,5–T. However, species such as live oak (*Quercus virginiana* Mill.) and huisache can be controlled by fall applications of picloram after susceptible crops such as vegetables, soybeans and cotton are harvested (13, 14, 15). Chemical drift from aerial sprays may damage susceptible species in adjacent cropping areas in spring and summer months. Granular formulations of picloram may minimize the drift hazard encountered with sprays, and it can sometimes be used in fall, winter and early spring months before susceptible crops are planted (14).

Picloram also controls a large number of herbaceous broadleaf weeds on rangelands and pastures in addition to brush.<sup>2</sup> Control of broomweed (*Gutierrezia dracunculoides* (DC.) Blake) may often be a concomitant benefit from spraying honey mesquite when 2,4,5-T + picloram are used (57). Common broomweed, controlled by low rates of phenoxy herbicides for a short period in the spring, may be controlled with 0.25 to 0.5 pound per acre of picloram through-

<sup>\*</sup>Research agronomist, Crops Research Division, Agricultural Research Service, U.S. Department of Agriculture, and assistant professor, Department of Range Science, Texas A&M University, College Station.

<sup>&</sup>lt;sup>2</sup>Ritty, P. M. 1967. Unpublished list. Susceptibility of plants to Tordon herbicides. The Dow Chemical Co., Midland, Mich.

out the growing season. Picloram also controls other herbaceous weeds which are resistant to 2,4–D or 2,4,5–T, such as western whorled milkweed (*Asclepiadaceae verticillata* L.) (46).

Chlorophenoxy herbicides, including 2,4–D and 2,4,5–T, dissipate rapidly in warm, moist soils. Klingman (41) stated that 1 to 3 pounds per acre of 2,4,5–T will last only 1 to 5 weeks under such conditions. Picloram is more persistent than chlorophenoxyacetic acid herbicides in soil (24, 48, 49). Some residual picloram may be necessary for control of several species of undesirable range and pasture plants. Huisache can absorb lethal concentrations of picloram through the roots or leaves (4, 7). Granular applications of picloram, by virtue of the herbicide's activity in soil,

TABLE 1. SOME PROBLEM WOODY SPECIES IN TEXAS AND THEIR RESPONSE TO SINGLE SPRAY APPLICA-TIONS OF PICLORAM, 2, 4, 5-T, OR MIXTURES OF PIC-LORAM PLUS 2,4,5-T<sup>1</sup>

	Controlled by-						
Species	Picloram	2,4,5-T	Picloram + 2,4,5-T				
Honey mesquite (Prosopis juli-		a gasaif	i ng sai si j				
flora (Swartz) DC. var. glan- dulosa (Torr.) Cockerell) Live oak (Quercus virginiana	yes	yes	yes				
Mill.) Post oak & blackjack oak (Quer- cus stellata Wangenh.) & (Q.	yes	no	yes				
marilandica Muenchh.) Macartney rose (Rosa bracteata	yes	yes	yes				
Wendl.) Winged elm (Ulmus alata	yes	no	yes				
Michx.) Cactus (pricklypear and tasajil-	yes	partial	yes				
lo) (Opuntia spp.)	yes	partial	yes				
Yaupon (Ilex vomitoria Ait.) Whitebrush (Aloysia lycioides	yes	no	yes				
Cham.) Blackbrush (Acacia rigidula	yes	no					
Benth.) Huisache (Acacia farnesiana	yes	partial	yes				
(L.) Willd.)	yes	no	yes				
Mixed hardwoods Texas persimmon ( <i>Diosypros</i>	yes	yes	yes				
texana Scheele) Spiney hackberry (granjeno)	no	no	no				
(Celtis pallida Torr.) Twisted acacia (Acacia tortuosa	yes	no	yes				
(L.) Willd.)	yes	no	yes				
Lotebush (Condalia spp.) Catclaw (Acacia greggii A.	no <sup>2</sup>	no	partial				
Gray) Agarito (Berberis trifoliolata	yes	no	yes				
Moric.) Lime prickly ash (Zanthoxylum fagara (L.) Sarg. (Z. pterota	no²	no	no				
(L.) H.B.K.)	no	no	no				
Yucca (Yucca spp.)	no	yes	no				

<sup>1</sup>Table prepared with the aid of G. O. Hoffman, Extension Range Brush and Weed Control Specialist, Texas A&M University, College Station. From Bovey, R. W. 1971. Hormonelike herbicides in weed control. Economic Bot. (In press). <sup>2</sup>Controlled with granular soil applications of picloram. can be used to control species such as huisache, live oak, yaupon (*Ilex vomitoria* Ait.) and whitebrush (*Aloysia lycioides* Cham.) (13, 14, 51). The present goal, then, should be to regulate the length of time that herbicides such as picloram are active in the ecosystem for maximum control of undesirable species and minimal damage to desirable species.

This report will summarize data available on the rate and routes of picloram dissipation from range land ecosystems and will report additional, unpublished data where appropriate. The discussion will include data from many sources to emphasize and explain research on Texas grasslands.

#### **Toxicity of Picloram**

"Picloram has a low order of toxicity to wildlife and fish" (44, 65). The test animals have included avian, mammalian and aquatic species (44). In studies of the biological food chain, algae-daphnia-fish, no adverse effects were observed from the introduction of picloram into the water (35). Research on 15 species of fish including rainbow trout (Salmo gairdnerii Richardson), channel catfish (Ictalurus punctatus Rafinesque) and bluegill (Leponis macrochirus Rafinesque), and on game birds such as mallards (Anos platyrhynchos) and bobwhite quail (Colinus virginianus) showed that herbicides containing picloram present a low potential hazard, if any, to wildlife and fish (39). Acute toxicity expressed as dosages lethal to half the test population  $(LD_{50})$  are greater than 750 milligrams per kilogram body weight for cattle and greater than 1,000 milligrams per kilogram for sheep (65). Approximately 6,000 milligrams per kilo gram is listed as the  $LD_{50}$  for chicks. Chronic toxicity to rats over a 90-day period requires dosages of 3,000 parts per million (ppm) (0.3 percent) for effects to be noted in liver. No effects were noted from 1,000 ppm (0.1 percent) over 90 days. Skin irritation or absorption of picloram through the skin is minimal.  $LD_{50}$  for rabbits by skin absorption was greater than 4,000 milligrams per kilogram. No corneal injury occurs from contact with eyes, and the resulting moderate irritation heals readily. There have been no known reports of human sickness resulting from the handling or application of picloram. It is generally concluded that the use of picloram presents no hazard to humans, livestock or wildlife. Moreover, the treatment of rangeland or of small grain fields with effective dosages of picloram would not result in levels of residue in food or feed toxic to humans or livestock (47).

#### Methods of Residue Detection

Picloram residues are usually determined by bio assay or gas-liquid chromatography (GLC). Bioassy methods, measurement of picloram concentration through the reaction of a susceptible organism, were described by Leasure (43). The most widely used procedure is to compare weights or symptoms of phyto toxicity of susceptible crops such as soybeans (*Glyane* max L.), sunflowers (*Helianthus annus* L.), field beam

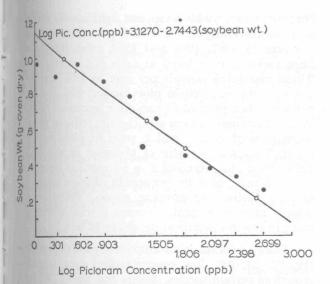


Figure 1. Example of a standard curve developed from soybean bioassay for determining concentration of picloram in field samples.

(Phaseolus vulgaris L.), or cucumbers (Cucumus sativa L) grown in field samples with those of plants grown in known picloram concentrations (18, 43, 60). Standard curves are developed with crop response versus dosage. Crop response in field samples is then converted to picloram concentration. A typical standard curve using ovendry weights of soybeans versus picloram concentration is shown in Figure 1. Rarely is the dose-response curve linear, regardless of bioassay species or method of evaluation (60). Using criteria such as dry weight of the assay species, a logarithmic relationship usually exists. Recent research describes a bioassay system using sesbania (Sesbania punicea var. Scorfield) for determination of picloram in the presence of 2,4,5–T in water (22). The high sensitivity of sesbania seedlings to picloram and insensitivity to low concentrations of chlorophenoxy herbicides makes the assay possible.

Merkle, Bovey and Hall (48) described extraction techniques for determination of picloram residues in soil samples by electron-capture, GLC. Twenty to 50 grams of soil are usually needed for this analysis. The method has gained wide acceptance and has been adapted to water and vegetation samples. The picloram is extracted from soil with equal volumes of a basic distilled water: methanol solution. The water: methanol extracts are evaporated to about 25 milliliters and are acidified. The acidified residue is extracted twice in ether and the aqueous portion discarded. Boron trifluoride: methanol reagent is then added, and the samples heated until only a trace of methanol remains. In the last step, picloram acid is converted to its methyl ester. Sample containers are then washed with distilled water followed by an equal volume of hexane. The water and hexane are combined in a separatory funnel, the aqueous portion discarded and one or two microliters of hexane injected into the gas chromatograph. Recorder response from the field samples is compared to that of known concentrations extracted by the above procedure (Figure 2). Recorder response is adjusted for extraction efficiency by adding known amounts of picloram to field samples and extracting by the above procedure. Usually, more than 80 percent of the picloram in soils can be recovered by the extraction procedure. Instrument temperatures, column materials and other details are given by Merkle *et al.* (48).

For analysis of water samples, 1 liter is evaporated to 100 milliliters, acidified with hydrochloric acid (HCl) and extracted with ethyl ether. The remainder of the procedure is as described for soils. Plant tissue is analyzed by grinding samples twice in acidified acetone. The suspension is then suction filtered, methylated and transferred to hexane in the same manner as described for soils.

Both bioassay and gas-liquid chromatography are useful methods of picloram detection, and results from soils are comparable (10, 60). Perhaps the most satisfactory procedure is to combine methods when possible. Determination of picloram residue in soil by GCL, verified by phytotoxicity to a susceptible crop,

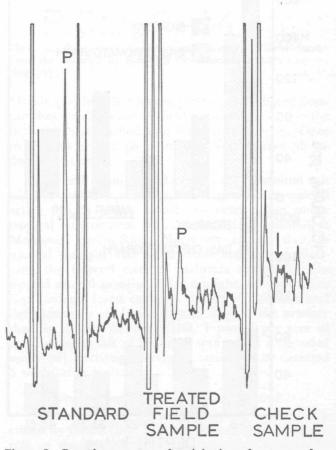


Figure 2. Recorder response after injection of extracts of a picloram standard, of a field sample treated with picloram, and of untreated field samples into electron-capture gas chromatograph. Concentration of picloram in field sample of soil is about 5 ppb.

leaves little question as to its presence. Bioassay and gas chromatographic techniques were compared in Figure 3 for Nipe and Fraternidad clays in Puerto Rico receiving 3 pounds of picloram per acre (10). Both methods showed similar trends in picloram concentrations at most depths of sampling.

#### **Picloram Residues and Susceptible Crops**

Most broadleaf crops are susceptible to very low rates of picloram. Alley and Lee (1) in Wyoming found that soybeans and other broadleaf crops showed symptoms of picloram in 1965 from applications of 0.5, 1, 2 or 3 pounds per acre in 1964. Near Alliance and North Platte, Nebraska, field beans failed to yield seed in 1966 where 2 to 5 pounds of picloram per acre were applied in 1964 to soils (20). Wiese<sup>3</sup> planted sorghum (RS 626) and soybeans (Clark 63) in June 1967, 1968 and 1969 in Pullman clay loam at Bushland, Texas, immediately, 1 and 2 years after application of picloram at rates up to 3 pounds per acre.

<sup>8</sup>Wiese, A. F. 1969. Unpublished data.

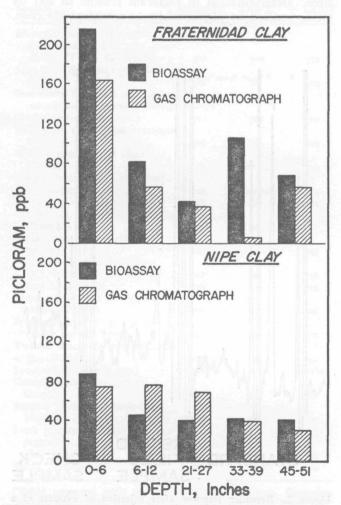


Figure 3. Comparison of cucumber bioassay and gas chromatography in determining picloram content in Nipe and Fraternidad clay in Puerto Rico 3 months after application of picloram at 3 pounds per acre. (Data from Bovey et al. (10)).

Sorghum grain yields were not significantly reduced in plots receiving 0.25, 2 and 3 pounds of picloram per acre in 1967, 1968 and 1969, respectively. Sobean yields were reduced at rates of picloram above 0.0156 and 0.125 pounds per acre in 1967 and 1968 but were not reduced in plots treated with 3 pounds per acre when planted 2 years after treatment in 1969. Wheat (Tascosa) was not significantly reduced in yield when planted after 1 and 2<sup>t</sup> years in plots receiving up to 3 pounds per acre of picloram in the fall of 1966. Most plots received 2 to 4 irrigation treatments of 3 to 4 inches of water per acre in addition to natural rainfall during the growing season. Picloram was usually present in small amounts 2 years after treatment in the soil profile at depths to 12 feet.

Since picloram is an auxin-like growth regulator (19, 23, 34, 38), low concentrations may stimulate growth of certain species. Scifres and Bovey (59) studied the reaction of seven varieties of sorghum seedlings to picloram in the greenhouse and found that the ovendry weights of some varieties were increased after treatment, some varieties were not affected and the growth of other sorghum varieties was reduced by relatively low picloram concentrations.

Bovey, Miller and Diaz-Colon (8) found that com, sorghum, wheat, rice and cotton could be grown with out reduction in fresh weight as early as 3 months after application of picloram up to 6 pounds per acre in a tropical environment in Puerto Rico. However, soybeans were more susceptible to residues and alter native cropping was suggested. Picloram, applied at one-half ounce per acre just before planting in Illinois reduced soybean (var. Harosoy 63) yields almost 40 percent (64). Picloram symptoms were notable on soybeans planted a year following application of 0.5 to 2 ounces per acre of picloram, but yields were not reduced.

Baur, Bovey and Benedict (6) found significant increases in the fresh weights of greenhouse-grown corn, sorghum, cotton, cowpea and soybean treated with water containing 0.25 to 0.5 part per billion (ppb) and wheat treated with water containing 100 ppb picloram. Herbicide treatment decreased soluble protein concentrations in aerial portions in the monocots studied and in sunflower. However, in cowpa and cotton, soluble protein was significantly increased by picloram treatment.

In Ohio (37) field studies, the relative tolerance of agronomic crops to picloram residues were com > barley > alfalfa  $\approx$  soybean. Two ounces (one eighth pound) per acre applied 9 months before planting had no visible effect on any of the crops. Picloram at 2 pounds per acre applied 9 months before planting had no affect on corn or oats, but reduced stands of barley by 40 to 50 percent and killed alfalfa and soybeans. However, neither yield nor stand of soybeans planted 20 months after application of 2 pounds per acre of picloram were affected. Klingman and Gueda (42) found that one-half gram per acre of picloram applied shortly after setting tobacco reduced the dollars returned from the crop by 50 percent.

Arnold and Santelmann (2) studied the effect of picloram on native grasses at various stages of growth in the field and in the greenhouse. Picloram applied preemergence at 0.75, 1.5 and 3 pounds per acre prevented the seedling growth of germinating blue grama and sideoats grama (Bouteloua curtipendula (Michx.) Torr.), big bluestem (Andropogon gerardi Vitman) and switchgrass (Panicum virgatum L.) When applied at the two and four-leaf stage at 1.5 pounds per acre, picloram significantly reduced the density of all species. However, picloram applied to established native range at rates up to 4 pounds per acre did not reduce production of desirable forage grasses. All treatments reduced production of forbs.

Studies in Nebraska (45) indicated that smooth bromegrass (*Bromis inermis* Leyss.) tolerated up to 0.25 pound per acre of picloram applied in the spring, but yields were reduced from the same rate applied in the fall. This response was correlated with root uptake of picloram by smooth bromegrass at initiation of vegetative growth.

Recent studies<sup>4</sup> indicate that 1 ppm of picloram in the upper inch of soil prevents the growth of sideoats grama and switchgrass seedlings.

However, in the field, native grass yields were significantly increased in plots receiving up to 4 pounds of picloram per acre in the subhumid areas of Texas as early as 6 months after treatment<sup>5</sup>. Sustained grass production was dependent upon effective brush control.

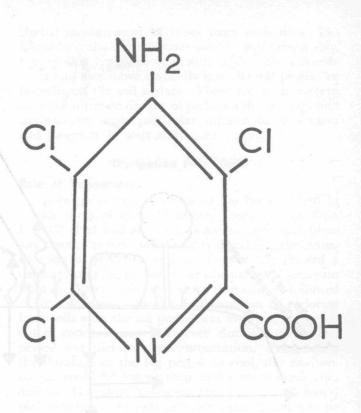
#### **Photolytic Degradation of Picloram**

Light in the ultraviolet range will degrade picloram molecules on plant or soil surfaces (30, 49). This reduces the amount of picloram available for movement in the ecosystem. The chemical structure of picloram is shown in Figure 4. According to Hall, Giam and Merkle (30), photodecomposition freed chloride ions, two for each picloram molecule degraded, and acids were formed in the process. The data indicated that the pyridine nucleus was destroyed by ultraviolet light. About 20 percent of a 2x10<sup>-2</sup> molar concentration was degraded per 48-hour exposure to ultraviolet light at 253.7 nanometers. Decomposition of the molecule occurred in sunlight but was slower and more variable than under controlled ultraviolet light sources in the laboratory.

The isooctyl ester of picloram was degraded more rapidly (96 percent) by ultraviolet light than the potassium salt formulation (26 percent) after 72 hours in open petri dishes under laboratory conditions (16). The rate of loss from esters applied to soil was lower than that from open petri dishes. Bovey, Dowler and

#### 'Scifres, C. J. 1971. Unpublished data.

Bovey, R. W., R. E. Meyer and H. L. Morton. 1970. Unpublished data.



## PICLORAM

Figure 4. Structure of picloram acid. Ultraviolet light decomposes the molecule by removing the chlorines and cleaving the ring (30).

Merkle (10) felt that loss of picloram by photodecomposition would occur in field applications unless the herbicide was leached into the soil (Figure 5). Once in the soil profile, picloram is protected from photodecomposition.

One milligram of picloram as the potassium salt (liquid) and 2 percent picloram granules remained active for at least 6 months in petri dishes under tropical environment and protected from rainfall at Mayaguez, Puerto Rico. Dishes were exposed daily to natural sunlight and forest shade conditions. However, the isooctyl ester of picloram completely dissipated after 6 months under sunlight, but not when kept under a forest canopy<sup>6</sup>. Hours of radiation and light intensity are less in Puerto Rico in the summer than in Texas. In Texas (10), 1 pound per acre of the potassium salt of picloram sprayed on a denuded sandy soil receiving no rainfall could not be detected 6 weeks after treatment.

#### **Vegetational Areas of Texas Studied**

Variation in the Texas environment has been discussed by Gould (26). Climate performs an important role in dissipating picloram. According to Gould's compilation, annual precipitation in Texas increases from west to east from about 8 inches at El Paso to

Bovey, R. W. and J. R. Baur. 1968. Unpublished data.

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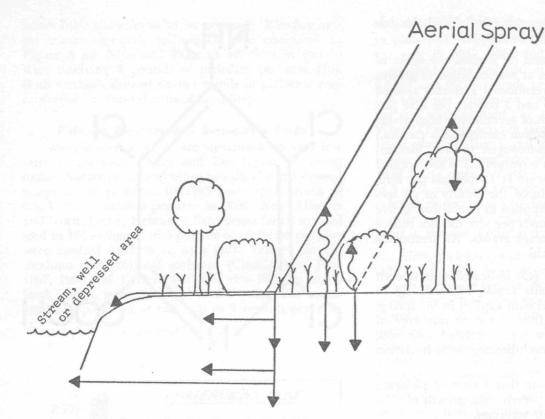


Figure 5. Theoretical routes of movement and dissipation of picloram after application to rangeland ecosystems.

over 55 inches at Port Arthur. Most of the precipitation comes as rainfall although snowfall contributes significant moisture in some areas of North and West Texas. The growing season increases from northwest to southeast with 179 frost-free days at Dalhart to 341 days at Galveston. According to Gould, Cenozoic clay and sand sediments influenced edaphic characteristics of the eastern and western thirds of Texas, whereas, central Texas was primarily influenced by limestones, marls, sands and clays of Mesozoic and Paleozoic eras. Gould recognizes 10 major vegetation areas of Texas (Figure 6).

Research on dissipation of picloram has emphasized several vegetational areas (Figure 6). One such area is the Rolling Plains, a southern extension of the Great Plains region of the central United States. This physiographic province occupies some 24 million acres, two-thirds of which is rangeland. Elevation ranges from 800 to 3,000 feet. Average annual precipitation is often less than 22 inches, and seasonal precipitation is highly variable. The province is characterized by hot, dry summer periods with high evaporation rates. Winter temperatures often drop below freezing. Soils are neutral to slightly calcareous, range from fine sands to clays and are all invaded by honey mesquite. Original vegetation included midgrasses. However, due to grazing pressure accentuated by periodic drouth, much of the area is presently shortgrass plains with a predominance of buffalograss (Buchloe dactyloides (Nutt.) Engelm.), tobosagrass (Hilaria mutica (Buckl.) Benth.) and blue grama (Bouteloua gracilis (Willd.) ex H.B.K.) Lag. ex Griffiths).

Two study sites were located in the Coastal Prairie, a slowly drained plain less than 150 feet in elevation. Average annual rainfall reaches 50 inches in the eastern portion and is fairly evenly distributed.

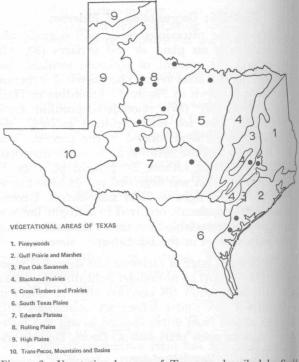


Figure 6. Vegetational areas of Texas as described by Gould (26). Black dots indicate locations where picloram dissipation studies have been or are being conducted.

The area is characterized by an average 300-day growing season, warm temperatures and high relative humidity. The soils are acid sands, sandy loams and clays. Slowly permeable soil profiles attribute to the formation of salt meadows and marshes. Climax vegetation is tall grass prairie but has been invaded by several species of brush. Tame pastures are common to the region.

A study area was also located in the Post Oak Savannah. Topography is gently rolling to hilly with elevation 300 to 800 feet. Annual rainfall is 35 to 45 inches with seasonal highs in May or June. The overstory species are blackjack oak (Quercus marilandica Muenchh.) and post oak (Quercus stellata Wangenh.) with tall grasses in the understory. The soils range from acid sandy loams or sands to clays. Improved pastures are widely used, especially following effective brush control.

The Blackland prairies are dark colored, calcareous clays supporting short, mid or tall grasses depending on latitude and site. The gently rolling to nearly level topography affords rapid surface drainage. Average annual rainfall varies from 30 to 40 inches from west to east. Vegetation typically would be true prairie, but much of the area is presently under cultivation or established in tame pastures.

The Edwards Plateau is located in Central Texas with elevations of 100 to more than 3,000 feet. Precipitation varies from 15 to 33 inches from west to east. Soil surfaces are rough, and profiles are shallow and underlain by limestone, caliche or granite. Brush overstory includes juniper (*Juniperus* spp.), honey mesquite, live oak and sand shinnery oak (*Quercus havardii* Rydb.). Rough rocky areas typically support a tall or midgrass understory grading into buffalograss and tobosagrass in the heavier, northwestern sites.

The South Texas Plains is located in the southemportion of Texas with elevations from sea level to 1,000 feet. Precipitation varies from 18 to 33 inches from west to east. The frost free period is 260 days in the north and 340 days or more in the south. The soils are dark calcareous to neutral clays with a firm clay subsoil. The bottomlands are silt clay loams of alluvial soils. The vegetation is a mixture of thorny woody plants and cacti.

#### Theoretical Routes of Dissipation of Picloram From Rangeland

Research on dissipation of picloram from rangeland ecosystems has been influenced by the information depicted in the flow chart in Figure 5. A typical, brush-infested range might consist of a woody plant overstory with low-growing shrubs and herbaceous plants in the understory. Most of the picloram released as an aerial spray will be intercepted by vegetational strata with the remainder reaching the soil or plant residue on the soil surface. Studies have included measurement of losses from such sites. Picloram formulations are water-soluble, and presumably, the applied herbicide is mobile within the environment and may move vertically into the soil profile, or laterally on the soil surface. There has been concern as to the ultimate destiny of picloram in the rangeland environment with particular interest to movement and longevity in soils and water supplies.

#### **Dissipation From Soils**

#### Role of Temperature

The persistence of picloram has been studied in a wide array of soils. Hamaker, Youngson and Goring (33) cited half-order reactions and Michaelis-Menton kinetics as most satisfactorily describing the detoxification of picloram in soils. Grover (27) showed a definite, early lag period in the dissipation of picloram from incubated soils after which degradation followed at first-order reaction. Thus, dissipation of picloram from soils after the lag period was over was independent of concentration. However, duration of the lag period was dictated by concentration. Presumably, the duration of the lag period in cool, dry environments would be longer than under more mesic conditions. Hamaker, Youngson and Goring (32) found picloram loss from soils collected from 18 states to be correlated with the number of days over 90° F and with annual precipitation. Thus, dissipation rates increased in the southern and southeastern states under prolonged, warm, moist conditions. Bovey, Ketchersid and Merkle (16) found that 45 percent of the isooctyl ester of picloram was lost from open petri dishes in a dark oven at 60° C, whereas only 2 percent of the potassium salt were lost. According to Merkle, Bovey and Davis (49), picloram dissipated more rapidly from Houston clay at temperatures of 38° C than at 4° or 20° C (Figure 7). Within a given temperature, picloram dissipation was more rapid at field capacity moisture than at 0.1 field capacity.

Although the specific role of temperature in the dissipation of picloram has not been established, the general conclusion by most researchers is that dissipa-

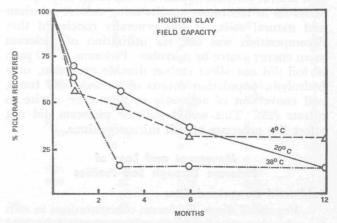


Figure 7. Dissipation of picloram from Houston clay as affected by temperature. (Data from Merkle et al. (49)).

tion is accelerated at higher temperatures. Since initial dissipation rates are concentration dependent, half-life values for different regions would be of little use (27). However, from a practical standpoint, residual life of picloram can be estimated with good accuracy based on degree and duration of temperature following application.

#### Influence of Soil Properties

Merkle et al. (49) reported that picloram was more persistent in clay or sandy loam than sand, attributing dissipation in light textured soils to removal by leaching. Grover (28) correlated the soil activity of picloram with pH and organic matter content but not with cation exchange capacity or percent clay. These data indicate that picloram is not inactivated by the soil colloids. Hamaker et al. (31) reported that sorption of picloram by soils was primarily due to organic matter and hydrated metal oxides. They also felt that clays were relatively minor in sorption of picloram. Both unionized picloram and the anion were involved in sorption on soils. However, Bovey and Miller (11) reported that up to 600 pounds per acre of activated charcoal was not sufficient to detoxify picloram after application of 0.5 pound per acre to a silty clay to allow growth of cucumber and field beans. Grover (28) also indicated that soil reaction, as influenced by ionic strength of the soil solution and organic matter, may influence phytotoxicity from residual picloram. This may indicate that availability of the acid or the salt form is important in the dissipation of picloram. Bovey et al. (16) illustrated relative stability of the salt formulation of picloram which indirectly supports this hypothesis. However, Youngson et al. (66) showed that pH and percent clay did not influence the rate of decomposition, but percent organic matter, percent moisture and temperature were important.

Little data are available substantiating microbial breakdown of picloram in soils. Resistance to microbial degradation may be responsible for the longer persistence of picloram in soils as compared to the rapid loss of 2,4-D. Youngson et al. (66) found that several varieties of bacteria and fungi decomposed picloram in laboratory studies using culture solutions and natural soils. It was generally concluded that decomposition was not via utilization of picloram as an energy source by microbes. Picloram at 100 ppm of soil did not affect carbon dioxide evolution, urea hydrolysis, population counts of bacteria and fungi, and conversion of ammonia to nitrate or nitrite to nitrate (25). This would indicate picloram did not affect life processes of soil microorganisms.

#### Movement and Loss of Picloram Through Soil Profiles

#### Subhumid Rangeland Sites

Vegetated Areas. Picloram concentrations in soils from brush research plots in Texas sprayed in 1963 and 1964 were determined with bioassay by safflower More frequent soil sampling at Victoria and Carlos indicated by gas chromatographic analysis that 2 pounds of picloram per acre disappeared from the top 2 feet of soil at 6 and 12 weeks after treatment, respectively (48) (Table 3). Picloram was not detected in soil from Victoria and Carlos after 1 year, regarless of application rate or sampling depth. To insurthat any variation within each plot would be detected, 25 samples from a plot sprayed with 8 pounds per acre of picloram were taken to a depth of 2 feet. Picloram residue was not detectable in any sample. As a further check, field beans planted in the same soils from Victoria and Carlos developed normally, indicating absence of residues.

Approximately 25 percent of the picloram reached the soil surface at Carlos and 10 percent at Victoria. Foliage of trees and other plants intercepted the spray. Dense stands of live oak covered the Victoria site, whereas the yaupon and herbaceous vegetation were more scattered at Carlos. Rapid disappearance of picloram from the light textured soils was partially attributed to leaching by rainfall (Table 4).

Additional studies were conducted at Carlos' to study picloram residues in soil after spray application of the potassium salt at 1 pound per acre. Picloram concentrations were usually less than 2 ppb at all levels down to 8 feet 1 year after treatment. Picloram levels ranged from about 1 to 10 ppb 6 months after treatment. The highest concentrations were associated with layers containing highest clay content at the 30to 36- and 66- to 72-inch depths. Cumulative rainfall at 6 and 12 months was about 16 and 28 inches, respectively.

Hoffman and Merkle<sup>8</sup> applied picloram:2,4,5T mixtures by airplane at 0.5+0.5 and 1+1 pounds per acre in 1966 and 1970, respectively, to a large area of mixed brush at Refugio. No picloram was detected in the heavy clay soil sampled to depths of 48 inches 150 days after spraying in spring 1970.

Fallowed Areas. Since part of the picloram spray is intercepted by vegetation and plant debris in vegetated areas, it was of interest to apply picloram to bare soils and investigate subsequent residues near Bryan and College Station (10) (Table 5). Picloram was applied to dry soil which received only trace amounts of rainfall during the first 6 weeks after treatment (Table 6). Loss of picloram was rapid during this period and can probably be attributed to photodecomposition. Picloram at 1 pound per acter

<sup>&</sup>lt;sup>7</sup>Baur, J. R. and R. W. Bovey. 1967. Unpublished data.

<sup>&</sup>lt;sup>8</sup>Hoffman, G. O. and M. G. Merkle. 1970. Unpublished data

#### TABLE 2. DESCRIPTION OF STUDY LOCATIONS, APPLICATION RATES, SAMPLING DEPTH AND SAMPLING SCHED-ULE WHERE PICLORAM CONCENTRATIONS IN SOIL WERE LESS THAN ONE PART BILLION AFTER TREATMENT OF BRUSH INFESTED RANGELANDS<sup>1</sup>

							Samp	oling
Location <sup>2</sup>	Site	Predominate woody species	Soil type	Annual precipitation (inches)	Picloram rate (lb./acre)	Date applied	Maximum depth (ft.) <sup>3</sup>	Months after treatment
Refugio (Gulf Coast Prairie)	1	Honey mesquite — huisache	Miguel f.s.l.	35	1,2&4	AICA	0	in the second
Coast Frame)	2	Honey mesquite — huisache	f.s.l. Miguel f.s.l.	35	1,2&4	4/64 10/63	3	14 11
Victoria (Gulf	1	Live oak	Katy			pol		
Coast Prairie)	2	Live oak	gravelly s.l	. 30	1&4	10/63	2	22
		Live oak	Katy gravelly s.l	. 30	2&4	4/64	2	16
	3	Live oak	Katy gravelly s.l	. 30	2&8	10/64	2	10
Carlos (Post Oak Savannah)	1	Yaupon, winged elm, post and blackjack oaks	Axtell f.s.l.	30	8	4/64	2	17
Carlos (Post Oak Savannah)	2	Yaupon, winged elm, post and blackjack oaks	Axtell f.s.l.	30	2	10/64	2	10
Edge (Post Oak Savannah)	1	Yaupon, winged elm, post and blackjack oaks	Axtell f.s.l.	30	1&2	5/64	3	15
Llano (Edwards Plateau)	1	Whitebrush	Gravelly s.l. <sup>4</sup>	29	1,2&4	10/63	2	22
	2	Whitebrush	Gravelly	00	1.00.4	FICA		
	3	Whitebrush	s.l. Gravelly	29	1,2&4	5/64	2	14
			s.l.	29	2&4	8/64	2	11
	4	Whitebrush	Gravelly s.l.	29	1,2,3&4	10/64	2	14
	5	Whitebrush	Gravelly	29	1,4,384	10/04	2	14
			s.l.	29	1,2,3&4	2/65	2	7

Bovey, R. W., R. E. Meyer and F. S. Davis. 1965. Unpublished data.

Nearest town to study site and vegetational region as described by Gould (26).

"Soil was analyzed in foot increments from surface to maximum depth sampled.

Soil series not determined.

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TABLE 3. RESIDUES OF PICLORAM IN PARTS PER MILLION IN TWO TEXAS SOILS AS DETERMINED BY GAS CHROMATOGRAPHY<sup>1</sup>

		Depth	Time between application and sampling										
	Rate lb./acre		Immedi-	One	Weeks							(s	
Location		in inches <sup>2</sup>	ately	day		2	in all	6		12	1	26	52
College Station	0	1,6,12,24	0	0	a da	0	bons	0		0	( tool	0	0
	2	1	1.00	0.89		0.06		0		0		0	0
	2	6				0.13		0		0		0	0
	2	12,24						0		0		0	0
	8	1	2.02	1.54		0.16		0.06		0		0	0
	8	6				0.72		0.33		0.08		0.05	0
	8	12						0.18		0.16		0.06	0
	8	24			10.67			0.16		0.07		.05	0
Victoria	0	1,6,12,24	0	0		0		0		0		0	0
	2	1	0.22	0.39		.08		.08		0		0	0
	2	6				.05		0		0		0	0
	2,	12,24						0		0		0	0
	8	1 22.0	1.38	1.30		0.25		.24		.06		0.05	0
	8	6				0.06		.05		0.12		0.07	0
	8	12						.06		.06		0.11	0
	8	24						.05		.05		0.05	0

Average of eight determinations, 0 indicates less than .05 ppm (data from Merkle et al. (48). Plus or minus 1 inch.

TABLE 4. TOTAL INCHES OF RAINFALL AFTER TREAT-MENT AT EACH SOIL SAMPLING DATE AT THE NEAR-EST WEATHER STATION FOR STUDIES CONDUCTED IN 1964 AND 1965 NEAR VICTORIA AND COLLEGE STATION<sup>1</sup>

Period after treatment	Victoria	College Station		
Immediately	0	0		
1 day	0	0		
2 weeks	0.8	3.9		
6 weeks	1.2	5.9		
12 weeks	3.4	8.3		
26 weeks	8.8	15.9		
52 weeks	31.4	32.0		

<sup>1</sup>Rainfall data taken from Texas Crop and Livestock Service, USDA, Austin, Texas. Stations are approximately 10 miles from field plots. (Data from Merkle et al. (48)).

disappeared from the sandy soil after 3 months. Picloram content was considerably reduced in sand and clay soils, after receiving 9 and 12 inches of rainfall, respectively.

Picloram applied to clay soil at 1, 3 or 9 pounds per acre was present in the upper 6, 12 and 36 inches of the profile, respectively, after 6 months (Table 5). Picloram was detected at nearly all levels down to 4 feet in sand 6 months after the application of 3 and 9 pounds per acre. Thus, the interrelationship of soil texture, herbicide rate and rainfall evidently governed the degree and rate of picloram movement vertically through the profile where no vegetation was present.

Picloram was not detected 18 months after application of 1 and 3 pounds per acre to sand and 1 pound per acre to clay surfaces bare of vegetation (Table 5). Picloram at 0.03 ppm was detected only in the surface of the clay soil after application of 3 pounds per acre. Picloram was found in the top 2 feet of the clay soil after application of 9 pounds per acre. Most of the picloram, 0.11 ppm, was at the 3 to 4-foot depth in the sandy soil treated with 9 pounds per acre. This indicated the tendency of picloram to leach to the subsoil of sandy soils.

#### **Tropical Sites**

Vegetated Areas. Picloram residues in soil were monitored at three sites by Dowler, Forestier and Tschirley (17) after application for woody plant comtrol in Puerto Rico. The studies were located in the Guanica Commonwealth Forest on Jacana clay, an alluvial soil normally less than 36 inches deep, with very low permeability. The vegetation is xerophytic with Leucaena leucocephala (Lum.) DeWit and Hae. matoxylon compechianium L. as the predominant woody species. The recorded annual rainfall at the site for 1964 and 1965 was about 28 and 25 inches, respectively. The Maricao Commonwealth Forest site was Nipe clay, a permeable, well drained lateritic soil derived from serpentine. The vegetation is a moist tropical forest. Rainfall for 1964 and 1965 was about 85 and 110 inches, respectively. The Luquillo National Forest site was Los Guineos clay loam, a plastic clay soil with poor internal drainage, supporting a tropical rain forest. Recorded rainfall was about 86 and 126 inches for 1964 and 1965, respectively. Picloram was applied with a hand spreader as granules, pellets, wettable powder or liquid absorbed on vermiculite. Applications were made October 1963 at Guanica, December 1967 at Maricao and January 1964 at Luquillo. Three months after application, picloram had moved downward in the soils to the 36 to 48-inch depth. The persistence of picloram generally was greatest in the driest area (Guanica) and least in the wettest area (Luquillo). One year after application, the picloram residue in plots treated with 27 pounds per acre remained at relatively high con-

TABLE 5. PICLORAM CONCENTRATION (PPM) DETECTED BY GAS CHROMATOGRAPHY IN ERVING CLAY LOAM AND LAKELAND SAND NEAR BRYAN AND COLLEGE STATION, RESPECTIVELY<sup>1</sup>

		Gas chromatographic analysis										
Picloram	Depth	Im	mediate	edly	1.204		3 mont	hs	6 mo	onths	18 n	nonths
rate (lb./acre)	sampled (inches)	clay		sand		clay	0	sand	clay	sand	clay	sand
1	0-6	0.76		0.48		0.15		0	0.02	0	0	0
	6-12					0		0	0	0	0	0
	12-24					0		0	0	0	0	0
	24-36					0		0	0	0	0	0
	36-48					0		0	0	0	0	0
3	0-6	2.11		1.75		0.67		0	0.15	0.02	0.03	0
	6-12					0		0.04	0.14	0	0	0
	12-24					0		0.07	0	0.05	0	0
	24-36					0		0.06	0	0.08	0	0
	36-48					0		0	0	1.01	0	0
9	0-6	6.92		6.99		0.33		0.07	0.22	0.33	0.61	0
	6-12	0.04				0.13		0.12	0.21	0.01	0.17	0.01
	12-24					0.05		0.23	0.08	0.05	0.04	0.01
	24-36					0.03		0	0.01	0.06	0	0
	36-48					0		0	0	0.06	0	0.11

<sup>1</sup>Soils were sampled immediately 3, 6 and 18 months after treatment (Data from Bovey et al. (10))

TABLE 6. TOTAL RAINFALL (INCHES) RECEIVED IN TEXAS AND PUERTO RICO FROM THE TIME OF PIC-LORAM TREATMENT UNTIL THE SOILS WERE SAM-PLED FOR RESIDUE DETERMINATION<sup>1</sup>

90°	Te	kas	Puerto Rico							
Time of sampling.	Bryan	College Station	Las Mesas	Tres Hermanos	Lajas					
(months after	Erving clay loam	Lakeland sand	Nipe clay	Cantano sand	Frater- nidad clay					
3	12	9	18	31	5					
6	14	13	49	48	31					
12	29	28	69	77	32					
18	40	46								

<sup>1</sup>Data from Bovey et al. (10).

centrations at all test sites. Only 5 ppb or less of picloram was detected in plots 1 year after treatment with 9 pounds per acre. Residue data for all locations indicated a trend for rapid dissipation from the top 12 inches of soil and downward movement in areas of high rainfall.

Fallowed Areas. The loss of picloram was studied on three soils in Puerto Rico under different rainfall conditions (10). Vegetation on the experimental areas was destroyed by cultivation. Nipe and Fraternidad days and Catano sand were studied near Mayaguez, Puerto Rico. Nipe clay is derived from serpentine rock and is high in iron content and low in fertility. This lateritic soil contains more than 70 percent clay of colloidal size but exhibits the physical properties of a loam. Water penetrates rapidly and is retained poorly. Fraternidad clay is brown, calcareous and heavy with lime accumulation at lower depths. Rock fragments occur to about 4 feet. The subsoil contains some salt and drains slowly after rainfall or irrigation. Catano sand occurs close to the ocean, usually at such a low elevation that the water table is within 18 inches of the surface. It is mapped as a poorly drained phase. The soil has a grayish-brown, friable, single-grained, sandy surface and a lighter textured, friable calcareous subsoil.

Three months after treatment, picloram was distributed throughout the soil profile in the clay soils after application of 1, 3 or 9 pounds per acre (Table 7). Picloram concentration increased as the rate was increased. Picloram persisted in the clay soils for a year, although the amount of picloram after application of 3 pounds per acre to Nipe clay was only 1 ppb at the 45 to 51-inch depth. Picloram was most persistent in the Fraternidad clay where rainfall was lowest. Disappearance of picloram from the Catano sand was rapid. No picloram was detected 6 months after treatment in the upper 3 feet of soil. Abundant rainfall apparently leached picloram from the soil.

Dowler et al. (17) found that the herbicides (2,3,6trichlorophenyl)acetic acid (fenac) and 2,4-bis(isopropylamino)-6-methoxy-s-triazine (prometone) were more persistent than picloram in a Jacana clay at Guanica, Puerto Rico, 1 and 2 years after treatment. Both compounds were leached to at least 4 feet and were distributed throughout the upper soil profile. The presence of vegetation on the treated areas usually reduces picloram residues in soils because it intercepts some of the sprays.

Lateral movement of picloram was indicated in studies in high rainfall areas by small amounts of picloram sometimes found in untreated areas adjacent to plots receiving high rates of picloram. However,

TABLE 7. PICLORAM CONCENTRATION (PPB) FROM VARIOUS DEPTHS OF THREE SOIL TYPES AFTER TREAT-MENT WITH 1, 3 AND 9 POUNDS PER ACRE NEAR MAYAGUEZ, PUERTO RICO1

		3 mo	nths after trea	atment	6 m	onths after trea	atment	12 m	onths after t	reatment
Soil	Depth sampled	P	icloram lb./ac	cre	1 129	Picloram lb./ad	cre	1	Picloram lb./	acre
type	(inches)	1	3	9	1 10	3	9	1	3	9
Nipe										No. In St.
clay	0-6	2	88	372	0	1	883	0	0	1
100	6-12	9	46	413	0	5	612	0	0	9
	21-27	3	41	243	3	9	215	0	0	2
	33-39	5	43	343	3	10	62	0	0	6
	45-51	11	42	190	8	16	109	0	1	8
Fratern	idad									
clay	0-6	32	215	883	2	520	846	0	178	525
	6-12	7	82	692	3	5	187	0	4	222
	21-27	24	42	377	8	218	729	0	1	48
	33-39	180	106	98	15	224	575	0	1	49
	45-51	55 2	69	225	23	218	729	1	2	198
Catano		1								
sand	0-6	0	0	0	0	0	0	0	0	0
	6-12	0	0	11	0	0	0	0	0	0
	21-27	1	1	2	0	0	0	0	0	0
	33-39	0	3	3	0	0	0	0	0	0

Suil samples were taken 3, 6 and 12 months after spraying. (Data from Bovey et al. (10)).

this could have been due to surface movement of picloram by runoff water after heavy rainfall.

These and other studies indicate that leaching by rainfall in subhumid and tropical environments is one of the most important means of picloram disappearance from upper soil profiles. Loss by leaching is most rapid from sandy soils and slowest from heavy clay soils. Photodecomposition may also be important, especially if picloram is exposed on soil and plant surfaces for extended periods. Further study is needed to determine loss of picloram by chemical or biological degradation in the soil profile.

#### **Semiarid Sites**

Field studies conducted in the Rolling Plains of Texas showed that detectable residues of picloram were usually restricted to the upper 12 to 18 inches of soil following application of one-fourth pound per acre with a truck-mounted sprayer (50) for honey mesquite control (56). The soils were sandy loam and the picloram was applied prior to the dry summer months. Irrigation was used to evaluate the role of leaching in distributing picloram in these soils. After application of up to 8.9 inches of irrigation over a 15-hour period within 20 days after picloram treatment, residues were usually not detectable below 18 inches. Since initial rates were relatively low (0.25 pound per acre), a relatively slow rate of loss would be expected. Dilution of the picloram by the soil mass may be an important mode of dissipating low concentrations. Picloram was usually dissipated from the soil profile within a year following application of 0.25 pound per acre to seven rangeland sites in the Rolling Plains of Texas.

Where 0.5 pound per acre was applied in 1965 in the Rolling Plains, picloram residues were not detected by bioassay at any soil depth to 30 inches in 1968 (Table 8). The soils were sandy, varying from 61 percent sand in the top 6 inches to 44 percent in the 18 to 30-inch zone. Picloram residues detected in 1968, from soils treated in 1967, were fairly uniform to 30 inches. The soil treated in 1967 was much lower in sand content than that treated in 1965. The soil treated in 1968 was intermediate in texture between those of the 1965 and 1967 locations, and picloram was detected to 42 inches where 0.5 pound per acre was applied.

TABLE 8. PICLORAM CONCENTRATIONS (PPB) AS DETECTED BY SOYBEAN BIOASSAY IN AUGUST 1968 AFTER THE APPLICATION OF A HALF POUND PER ACRE IN MAY 1965, 1967 OR 1968 AT THREE LOCA-TIONS IN THE ROLLING PLAINS OF TEXAS

Year of		Sampling 2	Depth (inche	es)
treatment	0 to 6	6 to 18	18 to 30	30 to 42
1965	0	0	0	6.2
1967	1	2	4	
1968	11	3	2	5

picloram through the soil profile is much less in the western portions of Texas than in the subhumid a tropical areas. The hot, dry periods following treament allow exposure of picloram for considerable lengths of time on soil surfaces. Photodecomposition is probably important in dissipating picloram from semiarid areas.

Hoffman<sup>8</sup> collected soil to depths of 30 inches

from rangeland treated with 0.5+0.5 pounds of pie

#### Influence of Slope on Distribution Of Picloram in Soil Profiles

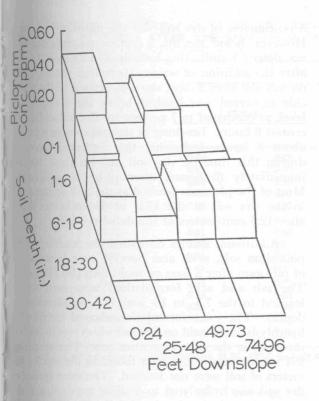
According to Scifres et al. (56), no significant in creases in detectable picloram occurred at the lower ends of plots until slope was increased to 3 percent in the Rolling Plains of Texas. Soil samples were taken 19 weeks after the application of 0.25 pound per are. Picloram did not accumulate at the lower end of 3 percent slopes at three locations in the upper 18 inches of the soil profile 1 year after the application of 0.25 pound per acre. In the same area, application of 0.5 pound of picloram per acre to a 2-percent slope did not result in accumulation of picloram at the lower end after 5 months (Figure 8). Also, no residue was detected below 18 inches in this Abilene silty day loam, regardless of slope or application rate.

However, detectable residues were recovered from 18 inches deep almost 2 years after the application of 2 to 4 pounds per acre of pelleted picloram to a \$ to 4-percent slope near Mertzon in the northern portion of the Edwards Plateau (Figure 9). Picloram residues were determined in this soil by soybean bioassay (60). More picloram residue was detected 6 to 18 inches deep at the lower end of the slopes than in the uppr 6 inches of the profile. Almost three times more picloram was detected after 4 pounds per acre picloram were applied than where 2 pounds per acre were used These data indicate increased persistence of picloram when leached into the soil profile followed by extended periods without rainfall.

#### Persistence of Picloram in Soils

Data from tropical, subtropical and semiarid environments indicate soil texture and rainfall are important in the leachability of the potassium salt of picloram in soils. Under natural conditions, clay content functions to retard leaching of picloram out of soil profiles (48, 55, 63). Solubility of picloram in the soil solution is apparently important in rate of leaching. The potassium salt applied at 1 pound per acre moved downward and disappeared from the upper

<sup>8</sup>Hoffman, G. O. and M. G. Merkle. 1970. Unpublished data



### 0.5 lb/A Picloram - 2°/o Slope

Figure 8. Distribution of picloram 5 months after the appliation of one-half pound per acre to a 2-percent slope on Abilene silty clay loam in the Rolling Plains of Texas. profiles of several soils in south Texas and Puerto Rico in 12 to 18 months, especially under high rainfall conditions (10).

When picloram at 1 pound per acre was applied to bare sandy soils at College Station, Texas, and Mayaguez, Puerto Rico, it disappeared in 3 and 6 months, respectively, from the profile and may have leached to lower points than sampled in the profile. However, Walter, Bovey and Merkle (63) studied the downward movement of 1 pound of picloram per acre after application of 40 inches of simulated rainfall over a 3-month period in Lufkin sandy clay loam embankment. No water was collected below the slowly permeable subsoil 15 to 18 inches deep. Consequently, no picloram was found below this depth. After 1 year, picloram was not found at any depth at this location.

Youngson et al. (66) and Moffatt (52) have implicated microbiological breakdown of picloram, but this type of degradation is usually of lesser importance than picloram removal from soil profile by other factors, such as leaching.

Degradation of picloram on plant and soil surfaces by sunlight is important when no rainfall occurs after treatment (10, 16, 30 and 49). However, once rainfall occurs, picloram apparently penetrates the soil surface and further photodegradation is limited.

Herr, Stroube and Ray (36) found highest picloram concentration near the surface of heavy and medium textured soil after 9 and 15 months. How-

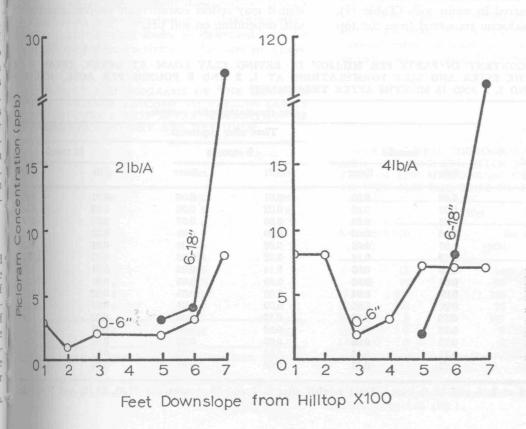


Figure 9. Distribution of picloram in the upper 18 inches of a 3 to 4-percent slope in the Edwards Plateau of Texas about 18 months after the application of 2 or 4 pounds per acre of pelleted picloram. ever, picloram moved through the top 2 feet of lighttextured soil with the greatest concentrations occurring at 18 to 24 inches. Scifres, Burnside and McCarty (55) detected more picloram after fall than after spring applications to pasture soils of Nebraska. More picloram was detected in the 24- to 36-inch depth from plots treated 1, 2 or 3 years before sampling than in plots treated the year of sampling, indicating accumulation in the lower portion of the clay soils. Research in Canada (40), a cooler climate than previously described, indicated that picloram was limited to the top 6 inches in four clay loam and loam soils. However, data on precipitation were not given. Frozen soil apparently restricted the downward movement of picloram in winter months. About 25 percent of the picloram persisted 12 months after treatment, but some was found 36 months after treatment.

#### Influence of Formulation on Residual Properties of Picloram in Soil

Initial studies compared the persistence of the isooctyl ester and the potassium salt of picloram in an Erving clay loam at Bryan and a Nipe clay at Mayaguez, Puerto Rico. It has been postulated that the ester of picloram, being less soluble in water than the salt, would not leach as readily in soil and would possibly be equally or more phytotoxic. Data in Tables 9 and 10, however, indicated that leaching patterns of the ester were similar to those of the salt. Each study area received rainfall soon after treatment.

In laboratory studies, the ester was applied to dry and moist soils 3 days before simulated rainfall. Considerable leaching occurred in moist soils (Table 11), whereas most of the picloram recovered from the top 5 centimeters of dry soil was the unhydrolyzed este However, below the top 5 centimeters, only the acid was detected, indicating hydrolysis of the ester to acid after the addition of water. Hydrolysis was increased on wet soil after 3 days, since 45 percent of the hether cide recovered was leached below the 5 centimetr level, as compared to 7 percent for dry soil and 8 per cent at 0 hours. Leaching of the soil column required about 8 hours, indicating that hydrolysis occured during this time on dry soil and on those leached immediately (0 hours) after picloram application. Most of the picloram leached as the acid accumulated in the wet soil at the 17.5- to 30-centimeter dept after 12.5 centimeters of simulated rainfall.

Additional studies compared the leaching of the potassium salt, acid, and isooctyl ester formulations of picloram after 3 days on moist soils (16) (Table 12). The salt and acid formulations were most readily leached to the 7.5- to 15- and 17.5- to 30-centimeter depths. The ester formulation showed considerable hydrolysis to the acid on wet soil which readily leached throughout the top 45 centimeters. The remaining 391 micrograms of the ester found in the top 5 centimeters of soil were not leached. The ester applied to dry soil was hydrolyzed to a slight extent during the application of simulated rainfall. However, only a small amount leached, and most was restricted to the upper few centimeters of the soil column. The remaining ester portion did not leach.

It was not possible to distinguish between add and salt of picloram with the analytical methods used in these studies. Consequently, the acid values presented may reflect considerable concentrations of the salt, depending on soil pH.

TABLE 9. PICLORAM CONTENT IN PARTS PER MILLION IN ERVING CLAY LOAM AT BRYAN, TEXAS, AFTER TREATMENT WITH THE ESTER AND SALT FORMULATIONS AT 1, 3 AND 9 POUNDS PER ACRE. SOIL SAM-PLES TAKEN 1 DAY, AND 3, 7 AND 18 MONTHS AFTER TREATMENT<sup>1</sup>

			Gas chromatographic analysis										
Pic-					Time after	treatment							
loram rate	Depth sampled	3 mc	nths		7 mor	ths	18 r	nonths					
(lb./acre)	(inches)	Salt	Ester	S	alt	Ester	Salt	Ester					
1	0-6	0.08	0.09	0	.01	0.06	0.01	0.05					
	6-12	0.07	0.05	0	.02	0.06	0.00	0.12					
2	12-24	0.03	0.08	0.	.00	0.07	0.01	0.02					
	24-36	0.00	0.06	0.	.00	0.05	0.00	0.02					
	36-48	0.00	0.06	0	.00	0.05	0.01	0.07					
3	0-6	0.49	0.14		.12	0.06	0.01	0.02					
	6-12	0.20	0.06		.14	0.06	0.01	0.03					
	12-24	0.04	0.08		.05	0.06	0.01	0.04					
	24-36	0.07	0.04	0.	.00	0.05	0.02	0.02					
	36-48	0.02	0.05		.00	0.04	0.01	0.02					
9	0-6	0.46	0.24		.13	0.06	0.02	0.10					
	6-12	0.58	0.12		.09	0.06	0.01	0.03					
	12-24	0.23	0.06		.09	0.06	0.02	0.07					
	24-36	0.11	0.14		.02	0.05	0.01	0.05					
	36-48	0.03	0.05		.00	0.08	0.04	0.07					

<sup>1</sup>Ester of picloram applied at 2, 6 and 18 lb./acre. Total rainfall after 3, 7 and 18 months was 11.85, 21.19, and 74.42 inder respectively.

				Gas chromatogra	phic analysis		
		a and shirt	and moder and	Time after t	reatment	steller frind a	el trade a
Picloram rate (lb./acre) (inches)		3 m	onths	6 mont	ths	10 mo	onths
	(inches)	Salt	Ester	Salt	Ester	Salt	Ester
1	0-6	0.06	0.09	0	0	0	0
	6-12	0.05	0.04	0	0	0	0
	21-27	0.05	0.07	0	0	0	0
	33-39	0.05	0.01	0	0	0	0
	45-51	0.05	0.05	0	0	0	0
3	0-6	0.02	0.00	0	0	0	0
	6-12	0.01	0.03	0	0	0	0
	21-27	0.04	0.02	0	0	0	0
	33-39	0.04	0.03	0	0	0	0
	45-51	0.03	0.02	0	0	0	0
9	0-6	0.19	0.03	0.03	0	0.04	0
	6-12	0.18	0.04	0.02	0	0.02	0
	21-27	0.08	0.04	0.01	0	0.02	Ő
	33-39	0.08	0.02	0.01	0	0.01	0
	45-51	0.07	0.02	0	0	0	0

Total rainfall after 3, 6 and 10 months was 31.91, 48.42 and 53.60 inches, respectively.

Data presented suggest that high losses of the isoctyl ester of picloram may occur after it is sprayed on hot plant and soil surfaces exposed to sunlight. Consequently, less herbicide may be available for plant absorption, especially through the soil. On wet soils, hydrolysis of the ester of picloram to acid or salt form was not complete after 3 days' exposure, and considerable loss of the unhydrolyzed ester may result from high temperatures and sunlight degradation. If root absorption is an important factor in obtaining effective brush control, then losses as described may be responsible for reduced activity of the ester in Texas.

TABLE 11. TOTAL MICROGRAMS OF THE ISOOCTYL ESTER OF PICLORAM LEACHED TO VARIOUS LEVELS OF SOIL COLUMNS 3 DAYS AFTER APPLICATION OF 1,000 MICROGRAMS TO WET AND DRY SOILS<sup>1</sup>

Soil depth		Soil tre	Soil treatment				
(cm)	$0 hr^2$	Wet	Dry				
0-5	788	392	668				
5-7.5		9	33				
7.5-10		4	2				
10-12.5		1	1				
12.5-15		0	2				
15-17.5	24	74	2				
17.5-30	43	206	0				
82.5-45	0	19	0				
47.5-60	1	10	7				
Leachate	0	0	4				
Total	856	718	721				

Twe inches simulated rainfall applied, (Data from Bovey et al. (16)).

Picloram applied to wet soil, leached immediately after treatment, and sampled at end of leaching period which took about 8 hours. Loss of the potassium salt of picloram in the laboratory was insignificant at high temperatures ( $60^{\circ}$  C) and was less subject to sunlight (uv) degradation than the isooctyl ester (16). However, application of the ester in paraffin oil or high concentration of surfactant (5 percent) reduced losses and should be studied under field conditions. Wind velocities appear to have no influence on picloram losses at 25° C.

Under field conditions in Texas, the potassium salt of picloram was usually more effective than the isooctyl ester formulation for control of live oak, yaupon, winged elm, huisache and honey mesquite (16).

TABLE 12. TOTAL MICROGRAMS OF POTASSIUM SALT, ACID AND ISOOCTYL ESTER 3 DAYS AFTER APPLICA-TION OF 1,000 MICROGRAMS OF EACH FORMULATION TO WET AND DRY SOILS IN THE LABORATORY

Wet					Dry	
Soil depth Salt Aci			l Ester <sup>1</sup>		Ester <sup>1</sup>	
(cm)			(acid)	(ester)	(acid)	(ester)
0-5	15	110	164	391	378	656
5-7.5	10	32	20	0	92	0
7.5-15	274	461	166	0	0	0
17.5-30	901	360	70	0	10	0
32.5-45	2	50	161	0	22	0
47.5-60	0	0	0	0	0	0
Leachate	3	0	3	0	3	0
Total	1,211	1,012	din a	963	1	,161

<sup>1</sup>The ester columns were analyzed as the ester and acid. (Data from Bovey et al. (16)).

#### Movement of Picloram in Surface Water

Trichell, Morton and Merkle (61) studied movement of picloram in runoff water in small plots 24 hours after application. Loss of picloram was greater from sod than from fallow plots. Four months after application, picloram losses averaged less than 1 percent of that lost 24 hours after application. The maximum loss obtained for picloram, 3,6-dichloro-oanisic acid (dicamba) or 2,4,5-T was 5.5 percent and the average approximately 3 percent. The time interval from picloram application to the first rainfall was the deciding factor as to the amount of picloram that moved into the soil profile and/or the amount moved away from the point of application with surface runoff. Picloram removed with surface water may be leached into the soil profile at some point downslope or be isolated in surface water catchments (Figure 5).

Studies by Scifres et al. (56) indicated that picloram was moved in surface runoff when 0.25 pound per acre was applied in the Rolling Plains of Texas for control of honey mesquite. Irrigation the first few days following application of the herbicide resulted in 17 ppb detectable residue of picloram in surface runoff. Irrigation at 20 or 30 days resulted in less than 1 ppb of picloram residue in runoff water. Presumably, more picloram was available on the soil surface soon after treatment than at later dates.

Hoffman<sup>8</sup> collected runoff water from 30 watersheds, 1.5 to 160 acres in size, in the semiarid and subhumid areas of Texas. Rates of picloram:2,4,5-T mixture varied from 0.25+0.25 to 2+2 pounds per acre. In the subhumid area, the greatest concentration of picloram (184 ppb) occurred 7 days after application of 1+1 pounds of picloram:2,4,5-T following the first rainfall that produced runoff. After 6 months, picloram could not be detected in runoff water in treated plots. In the semiarid area (Del Rio), 19 ppb of picloram was detected on a 25-acre watershed 12 months after application of picloram:2,4,5-T at 0.65+0.65 pounds per acre. However, picloram was not detected 12 months after spraying on two other similarly treated watersheds in the same area.

Baur and Bovey<sup>9</sup> studied picloram residues from a 15-acre watershed treated with 1 pound per acre of the potassium salt of picloram near Carlos. Samples were collected directly below the treated area and in streams below the plots after each heavy rainfall. Picloram residues ranged from 9 to 168 ppb after heavy rainfall in runoff water adjacent to the plots within 4 days after treatment. Concentrations of about 5 ppb or less of picloram were found in runoff water after 3 months. About  $1\frac{1}{2}$  weeks, after initial treatments in April, no picloram was found at several locations in the streams from  $\frac{1}{2}$  to 2 miles from the treated area near Carlos. No picloram was detected

<sup>8</sup>Hoffman, G. O. and M. G. Merkle. 1970. Unpublished data. <sup>9</sup>Baur, J. R. and R. W. Bovey. 1970. Unpublished data. in runoff water after a 2.4-inch rainfall 10 months after treatment, regardless of sampling location.

Johnsen and Warskow<sup>10</sup> sprayed a 31-acre water shed in central Arizona with 1.7 pounds of picloram per acre in June 1965 with a helicopter. Less than 0.1 ppm were detected by bioassays in runoff water the first year after treatment. An estimated 0.03 pounds of the 53 pounds applied left the area during the first 18 months after treatment.

Davis et al.<sup>11</sup> applied pelleted picloram (10 percent) at 9.3 pounds per acre to a 2.1-acre drainage area in a 46.5-acre watershed in central Arizona. Most water samples were collected at a weir directly below the treated area through which the entire watershed drained. The highest concentrations of picloram (0.37 ppm) were collected at the weir 7 days after treatment, after a 2.53-inch rain. Since the picloramtreated area was only 4.5 percent of the total area drained, there was a possible 22-fold dilution in pic loram content. In 3 months, picloram usually occurred in trace amounts and could not be detected after 1 year. The investigators indicated movement of picloram into streams was related to rainfall duration and amount and that water from picloram-treated watersheds may cause damage to crops if used for irrigation.

Sheets and Lutz<sup>12</sup> studied the movement of picloram and several other herbicides in runoff water from small plots in North Carolina. They found low concentrations of 2,4-D, 2,4,5-T and picloram in runoff water from watersheds sprayed at rates (2 and 4 pounds per acre) used for herbaceous and woody plant control.

Barnett et al. (3) found that formulation was important in the movement of 2,4-D from fallow land. No such comparison is available with picloram.

#### Dissipation of Picloram From Impounded Water Sources

Research conducted in semiarid and subhumid environments indicated that most of the picloram was dissipated from impounded, natural water sources within a month to 6 weeks after its introduction (29). However, 1 to 2 ppb were detectable a year after application of 1 pound of picloram per acre to the ponds. In no case did treatment of areas adjacent to domestic water wells (30 to 150 feet deep) result in detectable residues of picloram in those wells Once picloram was moved into water catchments in the Rolling Plains, residues were detected for at least a year following treatment (56). There is general

<sup>&</sup>lt;sup>10</sup>Johnsen, T. N. and W. L. Warskow. 1968. Picloram residues from treatment of Arizona chaparral. Weed Sci. Sco. Amer. Abstr. p 77.

<sup>&</sup>lt;sup>11</sup>Davis, E. A., P. A. Ingebo and C. P. Pase. 1968. Effect of a watershed treatment with picloram on water quality. USDA, Forest Service Research Note RM-100. p 4.

<sup>&</sup>lt;sup>12</sup>Movement of herbicide in runoff water. Presented before the American Society of Agricultural Engineers, December 9-12, 1969. Chicago, Illinois.

agreement among workers that dilution is important in the dissipation of picloram from impounded water. Some feel photodecomposition is important in reducing picloram concentration in water. In the photolysis of picloram, certain levels of light energy are necessary for degradation of each molecule. Assuming light energy is randomly dispersed, then interception of photons by picloram molecules would be a random occurrence. In such a system, the degradation of picloram would be expected to occur rapidly at first then decrease as fewer molecules were available for light interception. Such dissipation curves were reported by Haas et al. (29) who found that most rapid dissipation occurred within the first 3 to 4 weeks following application of picloram to impounded water. In such a concentration-dependent system, more energy must be applied for degradation of the remaining herbicide molecule than required at higher picloram concentrations. Recent research supports this hypothesis<sup>13</sup>.

#### **Dissipation of Picloram From Grasses**

Morton, Robison and Meyer (53) indicated that the amine salt of 2,4-D, 2,4,5-T and dicamba disappeared from silver beardgrass (Andropogon saccharaoides Swartz), little bluestem (Andropogon scoparius Michx.) and dallisgrass (Paspalum dilatatum Poir.) at about the same rate. The apparent average half-life was 2 weeks. Disappearance of the three compounds was slower in sideoats grama. Rainfall was important in accentuating the disappearance of these herbicides.

Getzenduner, Herman and Van Giessen (21) studied picloram residues in grass from seven states at various time intervals after application. Residues of up to 200 ppm were detected immediately after treatment for each pound of picloram per acre sprayed on grass. In all experiments, the picloram levels decreased rapidly within 1 and 2 weeks after treatment, then remained relatively constant for 8 to 16 weeks. Residues from a granular formulation generally increased through a maximum near the eighth week after application, then dropped to a lower level within the following 8 weeks. Residues generally decreased 90 to 100 percent over the midseason level after 1 year. In most cases, grasses collected the following spring after treatment showed no picloram residues. Residue levels from granular applications were generally lower than from the liquid formulation. No bound form of picloram was found in grasses.

#### **Subhumid Areas**

Studies at Victoria (5) showed grasses treated with picloram at 0.5, 1 and 2 pounds per acre averaged 2,650 ppb of fresh weight 1 month after treatment. Detectable picloram was reduced to 10 ppb in these tissues 6 months after treatment. Picloram residues in grass at Carlos after application in May 1969 of 1 pound per acre as the potassium salt averaged 32, 14, 2 and 0 ppm at 5, 30, 180 and 365 days after treatment, respectively. Plots were resprayed in May 1970 using the same formulation and rate. Resulting residues in grasses 6 months after retreatment were 2.2 ppm which were similar to 1969 results.

Hoffman<sup>8</sup> found no picloram in grasses 170 days after spraying picloram:2,4,5-T at rates up to 1+1 pound per acre at three locations in Texas (Bryan, Lampasas and Refugio).

#### **Semiarid Areas**

Picloram was dissipated from grass, primarily buffalograss, at rates of 2.5 to 3 percent per day after application of 0.25 pound per acre for control of honey mesquite in the Rolling Plains of Texas (58). Thus, more than 90 percent of the picloram was dissipated from the grass tissue within 30 days after application. However, at one of the three study locations, the concentration of picloram was increased in grass tissue from the 30- to 60-day samples. The workers felt this increase was the result of root uptake from the soil since it occurred after a flush of new growth following fall rains. Recent data<sup>4</sup> from greenhouse and laboratory studies substantiate the importance of root uptake of picloram and residue levels in aerial portions of grasses. Getzenduner et al. (21) showed that comcentrations of picloram in grass tissue increased to a maximum level at about 8 weeks following application of granular treatment. These data could also indicate root uptake of picloram by grasses under field conditions, although the concentration decreased in tissue from the eighth to the sixteenth week. Uptake of picloram by grass roots could explain residues detected in grasses in 1968 after treatment in 1965 and 1967 with 0.5 pound per acre (Table 13). Root uptake was important in the reaction of smooth bromegrass to picloram in Nebraska (45). Dissipation of picloram from grasses was not affected by irrigation to surface runoff within 10, 20 or 30 days after picloram application in the Rolling Plains of Texas (56). Hoffman<sup>8</sup> usually found no picloram in grasses taken from 13 locations in the semiarid areas of Texas 150 days after treatment with picloram:2,4,5-T mixtures from

<sup>4</sup>Scifres, C. J. 1971. Unpublished data.

<sup>8</sup>Hoffman, G. O. and M. G. Merkle. 1970. Unpublished data.

TABLE 13. PICLORAM CONCENTRATIONS (PPB) RE-MAINING IN GRASS TISSUE IN DECEMBER 1968 AFTER APPLICATION OF HALF POUND PER ACRE OF PI-CLORAM IN JUNE 1965, 1967 OR 1968.

Year of treatment	Picloram concentration (ppb)
1965	4
1967	11
1968	233

<sup>&</sup>lt;sup>19</sup>Personal communication, Dr. J. R. Baur, Plant Physiologist, USDA, Agr. Res. Serv., Texas A&M University, College Station, Texas.

0.25+0.25 to 1+1 pounds per acre. Where picloram residues did occur, little or no rainfall had been received between treatment and sampling.

Grass tissue sampled 5 months after the application of various rates of picloram near Spur in July 1968 contained sufficient quantities of herbicide detected with bioassay (Figure 10). Bioassay was accomplished by grinding 10 grams of grass, mixing the tissue with 50 grams of soil and planting the mixture to soybeans. Bioassay of tissue treated with 0.06, 0.25, 0.5, 0.75 or 1 pound per acre picloram detected residues of from 20 to 110 ppb depending on the field rate. Analysis of the data indicated that the amount of residue in the grass samples was a semilog function of the field rate.

Grass tissue was collected from plants growing under the canopy of treated redberry juniper plants and from adjacent open spaces near Mertzon about 18 months after the application of 2 or 4 pounds per acre of granular picloram. The predominant grass species were little bluestem and sideoats grama. Grass collected from the upper end of the 4 to 5 percent, 500-foot slope was analyzed separately from tissue collected at the bottom of the slope. There was little

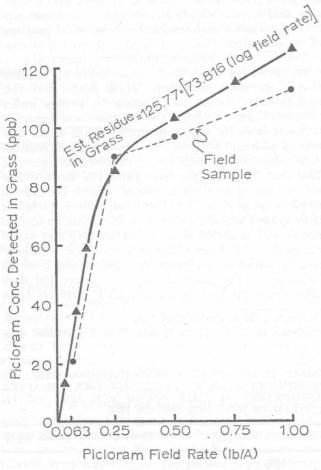


Figure 10. Concentration of picloram in grasses 5 months after the application of several rates in the Rolling Plains of Texas.

TABLE 14. HERBICIDE CONCENTRATIONS (PPB) REMAINING IN GRASS TISSUE IN 1968 AFTER THE APPLICATION OF 2 OR 4 POUNDS PER ACRE OF GRANULAR PICLORAM TO REDBERRY JUNIPER IN 1966 NEAR MERTZON, TEXAS

Position on hill	Relation of grass to	Picloram concentration (ppb)	
	juniper canopy	2 lb./acre	4 lb./acre
Тор	Under canopy	34	57
Тор	Open area	82	91
Bottom	Under canopy	29	140
Bottom	Open area	73	137

difference in the amount of detectable picloram in grass tissue collected from the upper and lower portions of the slope where 2 pounds per acre of picloram were applied originally (Table 14). However, grass tissue collected from under redberry juniper canopies contained less detectable picloram than grass growing in the open spaces where 2 pounds per acre were applied.

Approximately half as much detectable picloram residue remained in grass tissue from the top of the slope than at the lower end of the hill where 4 pounds per acre of the herbicide was used. Approximately half as much picloram was recovered from grass tissue sampled from under the redberry juniper canopies (57 ppb) than occurred in grasses sampled from adjacent open spaces at the upper part of plots treated with 4 pounds per acre. However, there was no difference in the amount of picloram recovered from grasses growing under the redberry juniper canopies and that growing in an adjacent open space at the lower end of the plot treated with 4 pounds per acre. Since the picloram was applied in pellet form, concentrations in aerial portions of grass tissue were undoubtedly due to root uptake. Analyses of soils showed highest amounts of detectable picloram at the lower end of this slope (Figure 9). These data indicate that position of the forage species in relation to the woody plants at time of treatment will affect the amount of picloram uptake by grasses.

### Dissipation of Picloram From Broadleaf Herbs

Scifres, Hahn and Merkle (58) reported that de tectable picloram was reduced by 93 percent in broad leaf plants within 30 days following picloram application. Since most of the leaves were killed by picloram, they became a part of the surface litter within 30 days after treatment. However, the deposition of the remains of the broadleaves to the surface debris did not increase picloram content in surface litter samples.

#### Dissipation of Picloram From Woody Species Subhumid Areas

Baur, Bovey and Smith (5) reported that amount of 2,4,5-T in live oak at Victoria were greater when applied in the presence of picloram than when 2,4,5T was applied alone. However, 99 percent of the herbicide detected at 1 month after treatment was dissipated 6 months later. TABLE 15. DISSIPATION OF THE POTASSIUM SALT OF PICLORAM APPLIED AT 2 POUNDS PER ACRE ON 4 TO 6FOOT TALL GUAVA IN JULY 1967, MAYAGUEZ, PUERTO RICO<sup>1</sup>

	Picloram (mg/g fresh wt.) Time sampled			
Plant part				
	(Immediately)	(1 month)		
Upper terminal		S. Second		
branches		0.51		
Upper leaves	654.3	0.76		
Upper twigs	121.9	0.38		
lower terminal				
branches		0.99		
Lower leaves	686.7	0.34		
Lower twigs	31.3	0.33		
Main stem	a for wood days danked or	0.55		

Three applications with two plants per replication with two composite samples per tree. Picloram applied during rainy

Baur and Bovey<sup>9</sup> studied picloram residues in erial portions and roots of yaupon in plots sprayed in spring 1969. Residues were usually less than 0.2 ym 180 days after spraying 1 pound per acre of pidoram but were not detectable 1 year after treattent. Plots were retreated in May 1970 with 1 pound yr acre of picloram. Six months after retreatments, radues in yaupon averaged 0.2 to 0.3 ppm, indicating little or no accumulation of picloram from 1 year in the next.

#### **Tropical Areas**

Guava (*Psidium guajava* L.) contained from 31 p687 ppm picloram in various plant parts after spraying with the potassium salt at 2 pounds per acre in Purto Rico<sup>6</sup> (Table 15). One month after treatment, pridues in all plant parts averaged less than 1 ppm.

#### Semiarid Areas

Honey mesquite leaves contained about 25 ppm picloram the day of application of one-fourth ound per acre. Leaves contained 0.3 ppm picloram the Rolling Plains environment (58). Time of irriation apparently had little affect on loss of picloram fom foliar tissue. According to Bovey and Diaz-Colon (12), herbicides applied in oil are difficult to rash from leaf surfaces with rainfall immediately after pplication. Picloram was more slowly dissipated rom sand shinnery oak leaves than from honey mesquite leaves (58). Deposition of honey mesquite leaves did not increase the picloram content of surface itter. However, the cumulative addition of remains of broadleaved herbs, honey mesquite and sand shinnerv oak leaves caused an increase in the picloram content of surface litter at 60 days, as opposed to 30 days after treatment.

\*Bovey, R. W. and J. R. Baur. 1968. Unpublished data. , "Baur, J. R. and R. W. Bovey. 1970. Unpublished data.

#### Acknowledgment

This study was a cooperative investigation of The Texas Agricultural Experiment Station, and Plant Science Research Division, Agricultural Research Service, USDA, Texas A&M University, College Station.

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