Reprinted from the *Journal of Weed Science*, Vol. 28, No. 5, September 1980. Pages 612-615.

Picloram Dissipation in a Small Southwestern Stream[1]

THOMAS N. JOHNSEN, JR. and WILLIAM L. WARSKOW[2]

Abstract. Picloram (4-amino-3,5,6-trichloropicolinic acid) injected directly into a small, central-Arizona stream was lost by normal stream flow actions, such as the mixing of fast- and slow-moving water, and the interchange of surface and subsurface water in gravel and sand beds along the stream. Picloram was injected at a concentration of 6.26 ppmw; the maximum amount detected was 2.362 ppmw at 0.4 km downstream, 0.943 ppmw at 0.8 km, 0.316 ppmw at 1.6 km, 0.014 ppmw at 3.2 km, 0.001 ppmw at 6.4 km, and none further downstream. Picloram was detected near the limits of detection (0.001 to 0.004 ppmw) 2 days after injection at the 0.4-, 0.8-, and 1.6-km sites. In photodegradation tests, sunlight decomposed 57% of the picloram in containers after 8.8 h of exposure.
Additional index words. Pesticide breakdown.

INTRODUCTION

The herbicide picloram controls a wide variety of woody plants. In the western United States it is being used to help restore livestock and wildlife forage production lost to brush invasion. As use of picloram on rangeland increases, it is important to know what happens to the herbicide in arid and semiarid regions.

Small amounts of picloram leave treated areas in surface runoff water (4, 5, 7, 8, 19, 21). However, little is known about what happens after it leaves the area (11, 20, 23). It is assumed that picloram dissipates because of dilution from additional incoming surface runoff water further downstream (4, 5, 7). In arid and semiarid regions, storms frequently are very localized and do not affect overland surface runoff downstream. Also, it is not known what could happen to picloram that might be released accidentally in small streams with no additional water to dilute the picloram.

This paper reports the disappearance of a known amount of picloram injected into a small stream located in semiarid southwestern pinyon-juniper and interior chaparral woodlands.

MATERIALS AND METHODS

Study area. The study was conducted on the lower 14.1 km of Tangle Creek, a tributary of the Verde River in central Arizona. Tangle Creek, a small, remote stream draining into a large body of water, is similar to many other drainages in the interior chaparral and pinyon-juniper woodlands of central Arizona. The stream had a relatively constant flow rate and a well-defined channel with shallow, sandy banks and sand bars on impervious bed rock. Estimated annual rainfall is 35 to 40 cm.

The day of treatment, March 25, was bright and clear with gusty winds. The stream water was clear, with filamentous algae growing along the stream edges. Riparian vegetation was just breaking out of winter dormancy near the injection point. Near the Verde River, the Fremont cottonwood (*Populus fremontii* S. Wats.) were flowering with leaves ¼ grown.

The velocities and volumes of flow were determined using a pygmy current meter in measured cross sections of the stream. A fluorescent dye (Uranin) was used the day before treatment to confirm the rates and patterns of water movement, and to determine the locations and timing of sample collections along the stream. Flow volume and velocity were measured during the treatment to detect any changes.

Treatment. A commercial herbicide, containing 0.12 kg/L ae of picloram and 0.24 kg/L ae of 2,4-D [(2,4-dichlorophenoxy)acetic acid] as the triisopropanolamine salts, was injected directly into Tangle Creek. The herbicide formulation was diluted with equal amounts of water to make 11.4 L of solution that was metered (22) into a flume carrying all of the stream's 0.036 m^3/s surface flow. The flume had specially designed baffling to insure rapid, thorough mixing of the herbicide solution and the stream water. The herbicide was injected into the stream for 50 min. Thus, a 1.46-km section of flowing stream water was treated to contain 6.26 ppmw of picloram and 12.52 ppmw of 2,4-D as the water left the flume.

Samples. Stream water samples were collected at seven locations downstream from the injection point the day the herbicide was injected (Table 1). A sample was also obtained 18 m upstream from the injection point. Additional samples were obtained 1 and 2 days after injection at the 0.4-, 1.6-, and 3.2-km locations.

Water samples were obtained by immersing a new 1-L plastic bottle at least three times through the deepest vertical profile of the stream at the collection point to obtain composite samples. The dip samples were sealed and kept in the dark after collection.

Single-stage flood water sampling stations (16) were installed at 1.6 and 14.1 km downstream from the injection point. One-liter plastic bottles covered with aluminum paint were placed at 15, 30, 45, 60, 75, and 90 cm above the normal stream flow level on a steel post. These and random dip samples were collected at 28, 56, 121, 170, 252, 517, and 546 days after injection. Bottles were replaced when collected or lost.

Soil samples from along the stream banks and sand bars were collected 2, 28, 56, and 121 days after injection by digging a shallow pit with a clean shovel at the 0.4, 0.8, and 1.6 km stations. Triplicate composite 500-g soil samples were collected in plastic bags in March and duplicate samples at other times. The soils were air dried as soon as possible after collection. Also, water accumulated in the holes was collected for assay. Sediments from around the single-stage sampling stations were collected in August and September the year following treatment.

Sunlight exposure. A composite stream water sample was collected 40 m below the mixing flume during injection to

[1] Received for publication August 14, 1979.

[2] Res. Agron., U.S. Dep. Agric., Sci. Ed. Admin., Agric. Res. Tucson, AZ 85719 and Supervisor, Watershed Div., Salt River Project, Phoenix, AZ 85001.

Table 1. Locations, sampling timing, and intensities of downstream water sample collections taken the day the herbicide was injected into the stream.

Location	Time sampling started[a]	Sampling intensity		Samples taken
		Duration	Intervals	
(km)	(h)	(h)	(min)	(no.)
0.4	0 + 0.33	1.0	5	13
	0 + 1.33	1.0	10	6
0.8	0 + 0.58	1.5	5	19
	0 + 2.08	1.0	10	6
1.6	0 + 1.17	4.0	10	25
	0 + 5.17	4.0	20	12
3.2	0 + 2.67	1.0	20	4
	0 + 3.67	1.0	10	6
	0 + 4.67	1.0	20	3
6.4	0 + 5.25	3.0	20	10
9.7	0 + 7.67	3.0	20	10
14.1	0 + 11.50	3.0	20	10

[a]Time after injection began.

determine the effects of sunlight on the picloram. The water was divided into eight 250-ml samples, four in plastic bags and four in shallow, wide-mouth glass jars. Paired duplicate samples were exposed to direct sunlight from 0810 to 1700 h March 25, with similar paired samples kept in the shade out of direct sunlight to serve as controls.

Assays. The content of picloram in water was determined by both biological and chemical assays; that in soils was determined by biological assays only. Initially, 15 safflower seeds were tested to determine samples needing dilution. Seeds were placed on the surface of 10 g of soil in a petri dish, watered with 10 ml of tap water, and placed in a germinator. After 72 h, seedling root and hypocotyl lengths were measured. Water was tested by placement of the seeds on filter paper to which was added 10 ml of sample water.

Soils were assayed biologically with 100 g of air-dried soil placed in a polystyrene cup. Eight soybean seeds were planted and watered with 25 g of tap water. Tap water was used for additional waterings. Plants were thinned to four per cup at the end of the first week. Soil dilution was done by uniformly mixing weighed amounts of dry, washed, fine quartz sand with air-dried soil to give the needed dilution series. Samples of known picloram concentration were made with similar but untreated soils by adding weighed amounts of technical grade picloram (98% purity), and diluting with soil to obtain the desired concentration levels. After 2 weeks the plants were compared visually with plants grown in known concentrations of picloram to determine herbicidal concentrations. Earlier tests with soybeans had indicated that 2, 4-D did not interfere with picloram detection when the commercial formulation was diluted to a level containing picloram concentrations of 0.016 ppmw or less. This agrees with other work (10). Therefore, all test samples were diluted as necessary to contain less than 0.02 ppmw picloram. The amount of 2,4-D was not assayed. This method is sensitive to as little as 0.004 ppmw picloram in soil. All tests were done with at least four replications. Biological assays were begun within a week of collection.

Water was bioassayed in a similar fashion by weighing 125 g of dry, washed, fine quartz sand into a polystyrene cup, planting the soybeans, and adding 25 g of test water. Known concentration series were prepared by adding weighed amounts of technical grade picloram to deionized water and diluting as needed. Sample dilutions were made by mixing weighed amounts of deionized and sample water to obtain the desired dilutions. The method is sensitive to picloram concentrations in water as low as 0.001 ppmw.

Water samples were also assayed by a commercial analytical laboratory using Dow Chemical Company's ACR 68.14 method of assaying for picloram with an electron capture gas chromatograph (method available from Dow Chemical Company, Midland, Michigan). This method is sensitive to 0.0004 ppmw picloram in water. Samples containing known amounts of picloram were used to confirm results along with the biological activity assays. All data reported for water samples are from gas chromatograph assays.

RESULTS AND DISCUSSION

Concentration of picloram in stream water. The highest concentration of picloram was 2.362 ppmw collected 0.4 km downstream from the injection point. This was 38% of the 6.258 ppmw picloram injected (Figure 1). The average concentration of picloram in the main body of contaminated water at 0.4 km was 1.630 ppmw (26%). The highest and average concentrations of picloram, respectively, further downstream were (Figure 2): 0.943 ppmw (15%) and 0.497 ppmw at 0.8 km; 0.316 (5%) and 0.282 at 1.6 km; 0.014 (0.2%) and 0.010 at 3.2 km; and 0.001 (0.02%) and 0.001 at 6.4 km. No picloram was detected at stations further downstream. No additional surface water entered the stream, and flow volumes were similar at each collection site. Dilution of picloram resulted from the normal process of the mixing of fast- and slow-moving water currents in the stream profile, and the interchanging of surface and subsurface waters in and out of gravel and sand beds along the stream channel. Such effects were also observed during the fluorescent dye trials, and are similar to the reported movements of other contaminants in streams (1).

When picloram was injected for 50 min, the leading edge of picloram-contaminated water was detected from 10 to 50 min before the peak levels appeared. The longest leading edge was at the 1.6-km site. Leading and trailing edges were not detected at the 6.4-km site, where picloram was found only at the limits of detection. However, it took about 1.5 h for the main body of water containing peak levels of picloram to pass each collection site. Picloram was not detected at other sites or in samples collected later, nor near the injection point after injection ceased. Picloram concentrations in the trailing edge were slightly higher at the 1.6-km site than at the other sites. This may have been due to picloram storage in a large, deep pool of still water and in a series of large sand bars just upstream from the 1.6-km station.

Results of the biological and gas chromatograph assays gen-

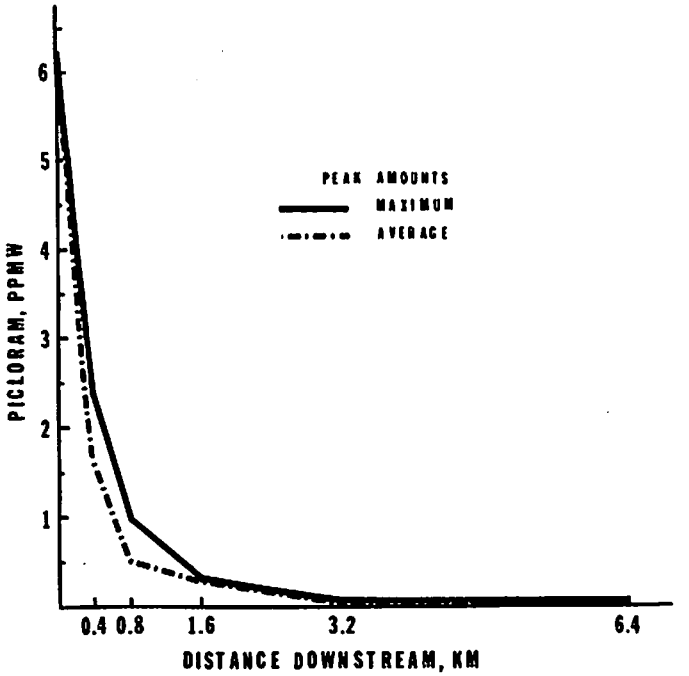

Figure 1. Relative amounts of picloram downstream from the injection of 6.26 ppmw picloram directly into Tangle Creek. Maximum peaks are the highest concentrations found at the site. Average values are the average of peak level concentrations of picloram in the contaminated water.

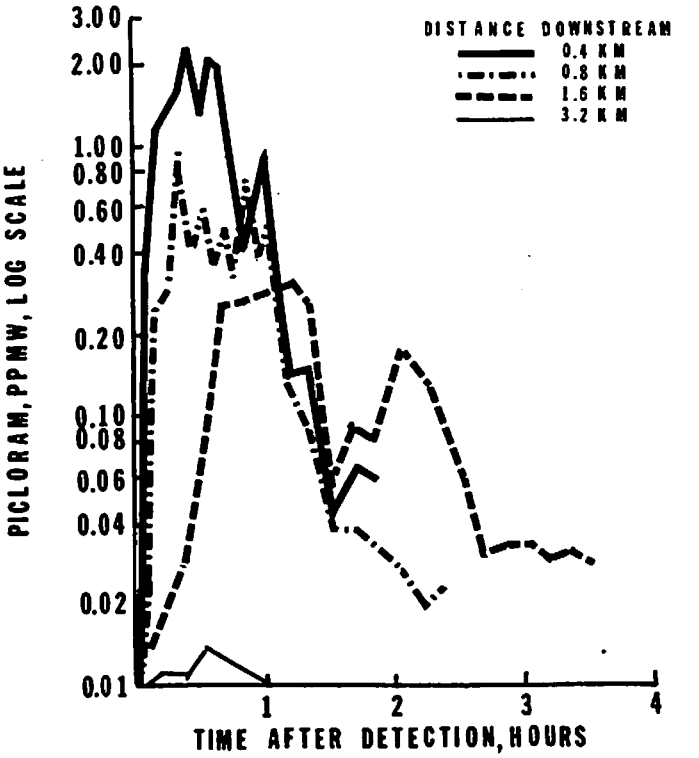

Figure 2. Picloram in stream water at various sampling stations during the sampling period after initial injection. Times begin with initial detection of picloram at the station. Picloram was also detected at the 6.2-km collection station, but was at the limits of detection of 0.001 ppmw.

erally agreed, showing the same trends. Biological assays varied from gas chromatograph assays mainly at the higher picloram concentrations.

Soil and soil water. Soil and water samples collected 1 and 2 days after injection contained small amounts of picloram. Soils had 0.500, 0.150, and 0.005 ppmw of picloram at the 0.4-, 1.6-, and 3.2-km sites, respectively. Water collected from the holes dug for soil samples contained 0.011, 0.006, and 0.001 ppmw at the same respective sites, and the concentrations were similar to those found in stream water collected at the same time. Muddy water contained slightly more picloram than did clear water. Picloram leaching from the soil accounted for the presence of small amounts of picloram in the stream water 1 and 2 days after injection. Picloram moves freely through sand soils (8, 18), but small amounts of clay and organic matter may retain some of the picloram. Also, the water flow is slowest near the bottom sides of the stream, so these are the last places to receive and release the picloram. Picloram was not detected in later soil sample collections. Similar results were observed with the fluorescent dye used to determine stream flow characteristics.

Sunlight exposure. Stream water after exposure to direct sunlight for 8.8 h contained 0.544 ppmw picloram or 43% of the amount found in unexposed stream water that contained 1.280 ppmw. Sunlight, mainly the ultraviolet portion, decomposes picloram (2, 15). The rapid breakdown in this study was unexpected. The results of other work indicates a much slower rate of picloram photodecomposition in sunlight (9, 14). There is probably more ultraviolet light of the short and most effective wavelengths at the 900-m elevation of Tangle Creek than at the lower elevations (12, 17), where the previous studies were done. The air mass over the study area was clear with no major air pollution sources nearby or upwind, resulting in minimal incoming radiation backscattering. Thus, the level of shorter ultraviolet wave lengths would be higher than in areas at lower elevations or areas with polluted air. This might also account in part for the high photodecomposition rate observed in this study.

Stream water contains salt, solid oxides, fluorescent pigments, and a variety of other substances, which can act to sensitize or desensitize photochemical processes (6), possibly also helping explain the rapid picloram loss observed.

Little picloram is lost by volatilization (14). There was no difference between concentrations in covered and uncovered containers in this study, and solution temperatures were not high enough to decompose the picloram. In the stream, picloram photodecomposition would be slower than in jars under controlled condition, because turbulence and partial shading by stream bank vegetation would reduce the amount of ultraviolet light penetrating into the stream water. Also, picloram entering soils along the stream would not be exposed to light. The rapid breakdown of the picloram in the jars might be related to the formulation used. Photodecomposition

rates of an ester were reported to be faster than those of a potassium salt (3, 5). However, the breakdown rate of the triisopropanolamine salt used would be expected to be closer to that of the potassium salt than to that of the ester. Photodecomposition is an important mechanism for loss of picloram from an aquatic environment (2, 14), and may be even more important in the high elevation rangelands and forest of the western United States.

Plant and animal responses. Little herbicide damage was observed on streamside vegetation the day following injection. Young stems on plants of yellow sweetclover [*Melilotus officinalis* (L.) Lam.] and an unidentified herbaceous forb growing adjacent to the stream up to 0.8 km below the injection point were slightly curved. Damage did not increase and growth was normal in later observations. Later in the spring, filamentous algal growth appeared less in the stream in the first kilometer below the injection point than above or below this portion of the stream. This could have been caused by differences in shade of water temperatures rather than by the herbicide. The filamentous algae may have absorbed some of the picloram and either metabolized it or slowly released it (22). The plants were not assayed for picloram content. Casual observation did not indicate any marked changes in the activity or apparent numbers of insects and small fish observed in the stream during or after the injection, which is in agreement with the observations of others (13).

Flood samples. No single-stage flood samples contained picloram. All above-normal stream flows overtopped the sampling stations. Debris indicated flood stages between 1 to 3 m deep were common, moving large amounts of soils and rock down the stream channel. Both single-stage sampling stations were washed out by a major storm a year after installation and were not replaced.

ACKNOWLEDGMENTS

The high level of performance, enthusiasm, and cooperation of the following individuals and companies made this study possible; Sid Wilson, Ken Vineyard, and Mark Tomlinson of the Salt River Project, Bob Warden and Jim Bean of the Dow Chemical Company; and Rey Madrigal, Sci. Ed. Admin., U.S. Dep. of Agric.

LITERATURE CITED

1. Bath, T. D., A. E. Vandergrift, and T. S. Hermann. 1970. Concentration profiles downstream from instantaneous pollution loadings. J. Water Pollut. Control Fed. 42:582–595.
2. Bovey, R. W., C. C. Dowler, and M. G. Merkle. 1969. The persistence and movement of picloram in Texas and Puerto Rican soils. Pestic. Monit. J. 3:177–181.
3. Bovey, R. W., M. L. Ketchersid, and M. G. Merkle. 1970. Comparison of salt and ester formulations of picloram. Weed Sci. 18: 447–451.
4. Bovey, R. W., C. Richardson, E. Burnett, M. G. Merkle, and R. E. Meyer. 1978. Loss of spray and pelleted picloram in surface runoff water. J. Environ. Qual. 7:178–180.
5. Bovey, R. W. and C. J. Scifres. 1971. Residual characteristics of picloram in grassland ecosystems. Tex. Agric. Exp. Stn. B-1111. 24 pp.
6. Crosby, D. G. and Ming-Yu Li. 1969. Herbicide photodecomposition. Pages 321–363 *in* P. C. Kearner and D. D. Kaufman, eds. Degradation of Herbicides. Marcel Dekker, Inc., New York.
7. Davis, E. A. and P. A. Ingebo. 1973. Picloram movement from a chaparral woodland. Water Resour. Res. 9:1304–1313.
8. Grover, R. 1973. Movement of picloram in soil columns. Can. J. Soil Sci. 53:307–314.
9. Hall, R. C., C. S. Giam, and M. G. Merkle. 1968. The photolytic degradation of picloram. Weed Res. 8:292–297.
10. Hamaker, J. W., H. Johnston, R. T. Martin, and C. T. Redemann. 1963. A picolinic acid derivative: A plant growth regulator. Science 141:363.
11. Hay, J. R. (ed.) 1974. Picloram: The effects of its use as a herbicide on environmental quality. Assoc. Common Sci. Criteria Environ. Qual. Nat. Res. Coun. Canada. NRCC no. 13684. 128 pp.
12. Koller, L. R. 1965. Ultraviolet Radiation. 2nd Ed. John Wiley & Sons, New York. 312 pp.
13. Lynn, G. E. 1965. A review of toxicological information on Tordon herbicides. Down Earth 20(4):6–8.
14. Merkle, M. G., R. W. Bovey, and F. S. Davis. 1967. Factors affecting the persistence of picloram in soil. Agron. J. 59:413–415.
15. Mosier, A. R. and W. D. Guenzi. 1973. Picloram photolytic decomposition. J. Agr. Food Chem. 21:835–837.
16. Rainwate, F. H. and L. L. Thatcher. 1960. Methods for the collection and analysis of water samples. Water Supply Pap. No. 1454. U.S. Geol. Survey Wash. D.C. 301 pp.
17. Reiter, R. 1968. The annual march and dependence of ultraviolet radiation on altitude in high mountains. Pages 51–54 *in* J. S. von Deschwanden, Karin Schram, and J. D. Thams, eds. Der Mensch in Klima der Alpen. Verlag Hans Huber, Bern.
18. Schneider, A. D., A. F. Wiese, and O. R. Jones. 1977. Movement of three herbicides in a fine sand aquifer. Agron. J. 69:432–436.
19. Scifres, C. J., H. G. McCall, R. Maxey, and H. Tai. 1977. Residual properties of 2,4,5-T and picloram in sandy rangeland soils. J. Environ. Qual. 6:36–42.
20. Smith, C. N., G. W. Bailery, R. A. Leonard, and G. W. Langdale. 1978. Transport of agricultural chemicals from small upland piedmont watersheds. EPA-600/3-78-056, May 1978. U.S. Environ. Prot. Agen., Athens, Georgia. 364 pp.
21. Trichell, D. W., H. L. Morton, and M. G. Merkle. 1968. Loss of herbicides in runoff water. Weed Sci. 16:447–449.
22. Turner, G. O. and A. Nilsen. 1967. Progress in the development of equipment for low volume application of liquid pesticides to soil. Down Earth 22(4):18–19.
23. Valentine, K. P. and S. W. Bingham. 1976. Influence of algae on amitrole and triazine residues in water. Can. J. Bot. 54:2100–2107.