

Altitude Effects on Picloram Disappearance in Sunlight¹THOMAS N. JOHNSEN, JR. and RICHARD D. MARTIN²

Abstract. Losses of picloram (4-amino-3,5,6-trichloro-picolinic acid) in water exposed to sunlight ranged from 50 to 80% after 1 days' exposure (14 h sunlight) and 95% or more after 4 days exposure (56 h of sunlight) at four locations in Southern Arizona. Samples exposed at the highest elevation (2800 m) consistently lost picloram more quickly than samples at the lower elevations. Dry, recrystallized picloram losses were 11, 47, and 67% after 1, 2, and 4 days of sunlight exposure, respectively. At the same times, picloram losses in water were 65, 89, and 99%, respectively. These results indicate that photodecomposition is an important factor for the use and residue longevity of picloram on high-altitude rangelands of the western United States.

Additional index words. Ultraviolet, rangelands, residues, photodecomposition.

INTRODUCTION

Picloram is being used to control brush and weeds on arid and semiarid mountainous rangelands in the western United States, where this herbicide could lie on the surface during lengthy dry periods following application. Such conditions effect soil applications of picloram (10). Sunlight decomposes picloram (8, 9, 11, 15, 16). Factors affecting such reactions have been reviewed elsewhere (4, 5). Solar-radiation intensities are uniform at altitudes below 300 m, but increase markedly with increased altitudes (2). Most work on the effects of sunlight on picloram has been done at altitudes below 300 m (8, 10, 11, 15, 16). One study (13), done at 900 m, reported a much faster picloram loss rate than previously reported, indicating that increased altitude may be an important factor. Because many ranges of the western United States are above 300 m in altitude, sunlight exposure may be very important if picloram disappearance rates accelerate with increased altitude. This paper reports the results of studies on increased-altitude effects on the loss rate of picloram exposed to sunlight.

MATERIALS AND METHODS

Study areas. The altitude trials were done three times during June 1979 near Tucson, Arizona, at four locations within 18 km of each other. Three fenced locations were provided by the Coronado National Forest on the Santa

Catalina Mountains north of Tucson: (a) near the top of Mount Lemmon, 2763 m, (b) near the Palisades Ranger Station, 2419 m, and (c) in Molino Basin, 1570 m. These locations are in heavily used recreational areas, the last two locations being adjacent to popular camp grounds. The fourth location was at the Carl Hayden Bee Research Center in Tucson at 720 m. Each site was leveled and exposed to direct sunlight throughout the day.

General weather data for Tucson and Palisades Ranger Station were obtained from the National Weather Service at Tucson. The summer rainy season prevented continued altitude trials. We did not measure the ultraviolet (UV) radiation because recording equipment could not be left unattended at the mountain locations. Spot UV reading would have been useless because of the large, unpredictable variation in radiation during each day at each site.

Sample preparation. Aqueous picloram stock solutions were made with 500 mg of analytical-standard picloram acid dissolved in 1000 ml of distilled water containing 15 drops of 6N NaOH, adjusting the pH to 7.0 with HCl. Test solutions containing 0.5 ppm (w/v) picloram were made for the first trial, but the concentration was increased to 1.0 ppm picloram for the remaining trials because of an unexpectedly rapid picloram loss. Both concentrations are similar to those found in runoff water from picloram-treated areas in Arizona (6, 12).

Individual samples were 150 ml of test solution in an air-tight bag made of plastic film³. The bags were less than 2 cm deep, thus 98 to 100% of the UV radiation received would be transmitted throughout the water solution and light path length had little effect (14).

Sample placement and collection. All samples were taken to the field in 0.5-L covered, cardboard, ice cream cartons at the beginning of each trial except for laboratory controls. Between 0900 and 1000 h, starting with the highest location, samples were placed 20 cm apart on a 1-cm-thick, 120-cm by 120-cm, white, styrofoam sheet fastened to the ground to standardize reflectance at each location. Controls to determine herbicide losses were unexposed bags of solution stored in darkness in the laboratory for each time period and the unexposed 0-day samples. We did not use shaded bags as controls because shading removes direct insolation, but not sky radiation; also, shading reduces solution temperatures.

Randomly selected triplicate samples were collected between 0900 and 1000 h at each location 0, 1, 2, and 4 days after starting each trial. However, only duplicate samples were collected in the second trial because of a mishap, which limited sample numbers. Each sample was placed into a covered ice-cream carton as soon as collected. Preliminary test results indicated that cold storage was not needed during transport. The remaining bags were wiped after each collection to remove accumulated dust.

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³ Saran-wrap was used for the first trial, but due to color changes with exposure to sunlight, subsequent trials were made with Handi-wrap. Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U.S. Dep. Agric. and does not imply its approval to the exclusion of other products that may also be suitable.

Sample assays. Samples were extracted the day of collection and analyzed within 72 h. The picloram was extracted from 100 ml of each sample by acidifying the solution with 3N HCl, extracting twice with 50 ml diethyl ether, then evaporating the ether to dryness. The dry extract was methylated by adding 3 ml diazomethane, heating until the yellow color disappeared, and then adding 10 ml distilled water. The picloram was recovered by placing the methylated solution into a separatory flask, adding 10 ml hexane, shaking 1 min, then letting the mixture separate, and saving the hexane layer by storing it over NaSO₄ to remove any trace of water.

The amount of picloram in each replicate sample was determined with an electron-capture gas chromatograph equipped with a ⁶³Ni electron capture detector⁴. The glass column was packed with 80 to 100 mesh absorbent⁵. A 95% argon, 5% methane carrier gas was used with a flow rate of 50 ml/min. Injector, detector, and column temperatures were 260, 280, and 220 C, respectively. Samples were compared with known concentration standards each day to correct for recovery variations. This test is sensitive to 0.0004 ppm picloram in water with typical recovery of 85 to 96%.

Dry-herbicide trials. The second set of experiments was done two times, once in July and once in August 1979 at Tucson. The dry picloram layer on 100-mm-diam petri dish bottoms was obtained by the method described by Baur et al. (1). The dishes were covered with a single layer of plastic film. Aqueous solutions were prepared as described before for comparison. The samples were placed on a styro-foam sheet on the Carl Hayden Bee Research Center roof and randomly selected triplicate samples collected 0, 1, 2, and 4 days after exposure began, as described before. Unexposed control samples were stored in the dark in the laboratory. The dry herbicide was recovered by washing the dish bottoms with 50 ml of basic distilled water (10 M KOH added to adjust to pH 10). The effluent was washed into volumetric flasks, brought to volume, then prepared and tested as described before.

Data assays. Day lengths during the June trials were ca. 14.25 h; day lengths were ca. 13.9 h during the July and August trials. Data were reported for days or multiples of the day length rounded to the nearest hour.

Data were analyzed for variance. Duncan's multiple range test was used to separate treatment means at the 5% level. Regression analyses were also used.

RESULTS AND DISCUSSION

Altitude trials. Marked picloram losses occurred quickly in aqueous solutions exposed to sunlight at each altitude tested (Table 1). Generally, there was significantly less picloram in exposed samples from the highest location than

from the other locations. After 1 day's exposure (14 h sunlight) losses ranged from 75 to 80% at the highest location and from 50 to 69% at the others in the three trials.

After 2 days (28 h sunlight) there was significantly more picloram lost in samples from the highest location, 91 to 94%, than from the lower ones, 82 to 86%, in the first and third trials (Table 1). In the second trial samples from the three higher locations lost significantly more picloram, 93 to 94%, than those from the lowest location, 89%.

After 4 days (56 h sunlight) 95% or more of the picloram was lost from samples at all four locations in each trial (Table 1). In the first trial, there was significantly less picloram left in samples from the highest location, 2%, and significantly more picloram left in those from the lowest location, 5%, than in samples from the other locations. In the second trial only a trace of picloram was found in samples from the highest location, damage to the bags caused leaks, which prevented meaningful assays of samples from the other locations. In the third trial, samples from the highest location had significantly less picloram left, 1%, than those from the three lower locations with 3 to 4%.

We do not show a strong relationship between increased altitude from 700 to 2400 m and accelerated picloram loss rates. However, the highest location, at 2800 m, consistently had greater losses than the lowest one and usually more than the other two locations. Variations in the rate of picloram disappearance from trial to trial and within each trial at a given location may be due to unpredictable sunlight variations during the day, between days, and from place to place (14).

Although the four locations are within 18 km of each other, differing elevations and proximity to metropolitan

Table 1. Average amounts of picloram remaining in aqueous solutions after exposure to direct light in three trials at four altitudes near Tucson, Arizona, in June 1979.

Trial date	Location	Altitude (m)	Exposure time (days) ^a			
			0	1	2	4 ^b
			————— (%) —————			
June 11 - 15	Lemmon	2800	100a	20a	7a	2a
	Palisades	2400	100a	36b	14b	3b
	Molino	1600	100a	33b	15b	3b
	Tucson	700	100a	31b	18b	5c
June 18 - 22	Lemmon	2800	100a	21a	6a	T
	Palisades	2400	100a	36b	7a	...
	Molino	1600	100a	40b	7a	...
	Tucson	700	100a	36b	11b	...
June 25 - 29	Lemmon	2800	100a	24a	9a	1a
	Palisades	2400	100a	38ab	18b	4b
	Molino	1600	100a	50b	14b	3b
	Tucson	700	100a	48b	17b	3b

^aData corrected for recovery. Means within each column of the same trial followed by the same letter are not different at the 5% level as determined by Duncan's multiple range test.

^bT = less than 1 ppb; ... = not determined.

⁴Tracor Model 222, Tracor Inc., Austin, TX.

⁵5% O/V - 1 on Gas-Chrom Q, Applied Sci. Lab., State College, PA.

Tucson result in marked differences in air pollution, clouds, rainfall, and air temperatures. The air at Tucson and Molino Basin is often polluted by dust, smoke, and automobile exhausts. Palisades, located near heavily used campgrounds, has smoke and dust pollution. Brush fires on lower parts of the mountain during the trials also caused smoke pollution at Molino Basin and Palisades. Mount Lemmon gets heavy hiker use, but little motor vehicle use and has little dust and smoke pollution. Dust and smoke particles in the air or on sample bags absorb and scatter UV light, reducing its intensity and energy levels (5, 14). When we cleaned the sample bags during collections, we noted little dust at Mount Lemmon and variable amounts at the other locations. Automobile exhaust is oxidized in the air and absorbs UV light, reducing its intensity (14). Rainfall, which is more frequent at the higher altitudes, removes many pollutants from the air, helping maximize sunlight intensities after the storm.

Air temperatures were 10 to 12 C warmer at Tucson than at Palisades, and a temperature of 50 C was measured under bags at Tucson on June 15. However, Michel et al. (16) reported marked effects of light intensities, but not temperatures, on picloram photodecomposition rates. Little effect of temperature on volatilization was observed by Bovey et al. (3) or Baur et al. (1) in their studies. Thus, temperature differences between the locations may not influence picloram loss rates.

Dry-herbicide trials. In the second set of tests, the amount of dry, recrystallized picloram was reduced by 11% after 1 day's exposure (14 h of sunlight), 47% after 2 days (28 h sunlight), and 67% after 4 days (56 h sunlight). During the same times, picloram dissolved in water was reduced by 65, 89, and 99%, respectively, similar to the June losses. Unexposed picloram had no changes. Although dry picloram was not lost as rapidly as picloram in water solution, it disappeared quickly. This indicates that picloram spray residues left on exposed surfaces of foliage, rocks, and soil could be quickly photodecomposed.

The loss rates we observed are faster than those reported from other studies done at lower elevations. For example, picloram crystals were reduced by 16 to 22% after 2 days sunlight exposure at 100 m in Texas (10). Picloram loss was 15% when exposed 7 days in preliminary tests at 300 m in Arizona⁶. In our current trials we observed a 47% loss of dry picloram in 2 days at 700 m. The loss rates observed in the present study are similar to the 57% lost after 9 h

exposure at 900 m in Arizona (13) and those reported from laboratory exposure of picloram to 300 to 380 nm artificial UV radiation (3, 9, 17), wavelengths that occur in sunlight.

Even the slowest breakdown rates we observed showed that exposing picloram to sunlight in the summertime on high-altitude range sites can be a major factor in the disappearance of this herbicide from that environment. Such breakdown may reduce effectiveness of the herbicide to control brush and weeds on high-altitude rangelands. These observations may also help explain the loss of picloram already observed on semiarid, high-altitude ranges (6, 12).

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