Picloram Movement in Soil Solution and Streamflow from a Coastal Plain Forest

J. L. Michael,* D. G. Neary, and M. J. M. Wells

ABSTRACT

Picloram (4-amino-3,5,6-trichloropicolinic acid) was aerially applied to a longleaf pine (*Pinus palustris* L.) site in the upper coastal plain of Alabama to control kudzu [*Pueraria lobata* (Willd.) Ohwi]. Pellets (10% a.i.) were spread at the rate of 56 kg ha^{-1} on loamy sand Typic Kanhapludult soils. Movement of this herbicide was monitored with mineral soil samples, tension-cup lysimeters, flow-proportional streamflow samplers, and discrete samplers. Picloram levels in the upper 15 cm of mineral soil peaked at 0.96 to 2.25 mg kg^{-1} 25 d after application, depending on slope position, and declined to 0.13 to 0.29 mg kg^{-1} 1 yr later. In soil solution, picloram was detected at a depth of 0.4 m between 26 and 273 d after application. Only 4 of 15 lysimeters consistently contained detectable residues. Maximum picloram levels in soil solution were 130, 450, and 191 mg m^{-3} for ridge, midslope, and toe-slope positions, respectively. Downstream monitoring began 4 d after the herbicide application, and an initial concentration of 68 mg m^{-3} of picloram was detected. The maximum downstream concentration of 77 mg m^{-3} occurred 18 d after the application, immediately after the second storm event. Downstream levels dropped to <10 mg m^{-3} after 90 d and to <2 mg m^{-3} after 200 d. Following localized retreatment along the stream more than a year after the initial treatment, levels climbed again into the 20 to 30 mg m^{-3} range. Most of the initial off-site movement came from a perennial stream that had been inadvertently treated, but subsequently storm runoff was the largest contributor to stream contamination. Picloram residues in this stream were similar to those observed downstream, but they were higher (up to 241 mg m^{-3} and dropped faster to below 2 mg m^{-3} after D 150.

KUDZU [*Pueraria lobata* (Willd.) Ohwi] is a perennial leguminous vine that has become a serious weed problem in the South since its introduction from Japan in 1876 (Shurtleff and Aoyagi, 1977). However, its rapid growth rate (10–20 m yr^{-1}) and habit of forming dense vegetation mats have made it useful in stabilizing eroded gullies and roadsides. But the growth characteristics of kudzu have enabled it to invade forests, smothering pines 25 m tall and making regeneration almost impossible. Because of the spread of kudzu via stolons and rhizomes, effective control can be accomplished only through elimination of the root system. Beginning with Davis and Funderburk (1964) and Brender and Moyer (1965), chemical treatment with picloram (4-amino-3,5,6-trichloropicolinic acid) pellets[1] has proven to be one of the most effective control measures.

Use of picloram in forest ecosystems has become controversial because of the persistence and mobility of the chemical (Norris, 1981a). Picloram is moderately to highly persistent in soils, with a half-life of 30 d in humid regions to over 400 d in arid regions (NRCC, 1976; USDA-FS, 1984). Because it is degraded by microorganisms, conditions that favor microbial activity result in higher rates of breakdown (Ghassemi et al., 1981). It is highly soluble (potassium salt >400 000 g m^{-3} at 25 °C) (Johnson, 1971) and is a very active growth regulator herbicide on a variety of plants. Picloram is generally low in mammalian toxicity (LD_{50} > 8000 mg kg^{-1} of body weight) (NRCC, 1976). Picloram movement in agricultural ecosystems is highly variable, depending on site conditions (Scifres et al., 1971; Trichell et al., 1968; Baur et al., 1972). Applications of picloram to forests in the Pacific Northwest at the rate of 2.2 kg ha^{-1} a.i. have generally produced low concentrations in streamflow (20-78 mg m^{-3}), and losses from those sites have been <0.3% of that applied (Norris, 1981b; Norris et al., 1982). A lower rate of picloram (0.9 kg ha^{-1}) for control of riparian vegetation in an Arizona forest watershed resulted in higher streamflow concentrations (370 mg m^{-3}) and longer persistence in the environment (Davis *et* al., 1968). In the Southern Applachians, picloram pellets applied at 5.0 kg ha^{-1} a.i. to remove hardwoods resulted in mobility in loamy sand soils down to 120 cm (up to 200 mg m^{-3}) but did not result in significant movement of residues into springs or stream systems (Neary et al., 1985).

The primary objective of this study was to quantify the movement of aerially applied picloram in an operational-scale use of the chemical in the upper coastal plain of Alabama. Specifically, the goals of the study were to determine (i) the amount of picloram leaching in sand-textured forest soils, (ii) the persistence of picloram in mineral soil, (iii) the off-site movement of this chemical in storm runoff and baseflow, and (iv) its movement downstream. In addition, sufficient replication was programmed into the study to provide information on the variability of picloram residues in the environment. This type of information is important for guiding subsequent monitoring of applications of this herbicide.

METHODS

Site Description

The study site is located within the Uphapee Creek watershed, in the Tuskegee National Forest in east-central Alabama. A subunit watershed, northerly in aspect and ranging from 82 to 137 m elev., contains the treatment area (Fig. 1). Slopes are dissected and complex, averaging 6% but exceeding 17% in some locations. The soils formed in medium-textured marine deposits and belong to the Cowarts-Uchee

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[1] Tordon® 10K Pellets Herbicide is manufactured by Dow Chemical Company, Midland, MI. Use of trade names here and throughout the text does not constitute endorsement by USDA but is provided as a reference. Discussion of herbicides in this paper does not constitute recommendation of their use or imply that uses discussed here are registered. If herbicides are handled. applied, or disposed of improperly, there is potential for hazards to the applicators, off-site plants, and environment. Use herbicides only when needed and handle them with care. Follow the directions and heed all precautions on the container label.

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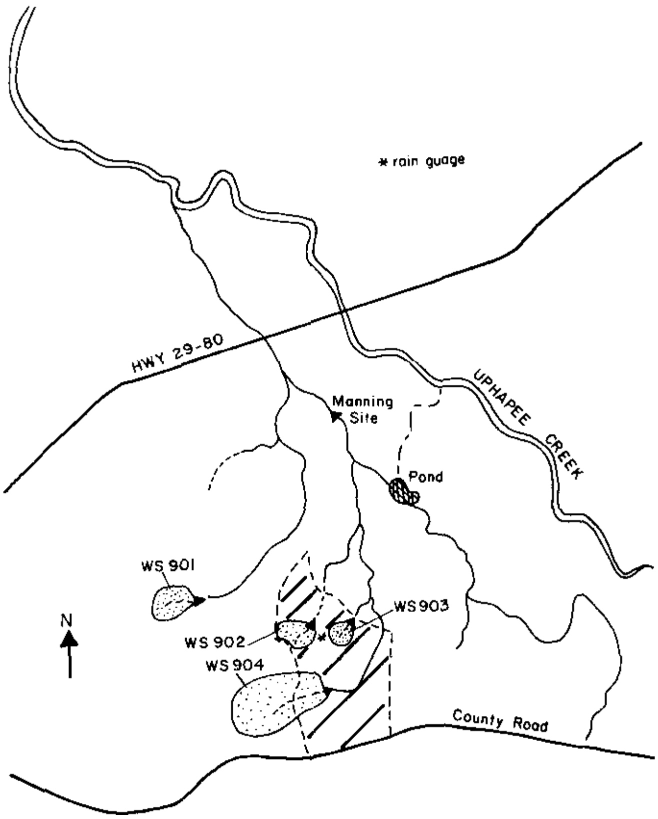

Fig. 1. Picloram application site (area outlined by dashed lines) in the Uphapee Creek watershed, Tuskegee National Forest, Alabama.

association. The broad ridges and slopes are Cowarts loamy sands (fine-loamy, siliceous, thermic Typic Kanhapludults). The colluvial soils along the broad ephemeral stream bottoms within most of the treated area are loamy sands of the Uchee series (loamy, siliceous, thermic Arenic Hapludults). Both of these soils are generally underlain by sandy clay loam argillic horizons at variable depths (0.2–1.0 m). Soil pH values range from 4.5 to 5.5 throughout the profile. Surface horizon organic matter is highly variable on disturbed forestry sites, but is generally < 1%.

The main forest overstory and much of the original understory were destroyed by wildfire in 1978. Longleaf pine (*Pinus palustris* Mill.) and loblolly pine (*P. taeda* L.) predominated on ridges with a site index of 70 to 80. Side slopes supported a variety of hardwoods and brush species. The stream bottoms were predominantly sweetgum (*Liquidambar styraciflua* L.), water oak (*Quercus nigra* L.), and yellow poplar (*Liriodendron tulipifera* L.). Following a salvage operation to remove the remaining timber, existing kudzu grew and spread rapidly from numerous crowns.

Instrumentation

Four watersheds (WS 901.904, Fig. 1) ranging in size from 1.2 to 4.1 ha were instrumented with H-flumes, Coshocton wheel flow proportional samplers, and analog water level recorders. The equipment was installed in March 1981 in configurations described by Brakensiek et al. (1979), Douglass and Van Lear (1983), and Neary et al. (1983). Of the three watersheds established within the treated area (WS 902-904), only WS 904 maintained perennial streamflow and only the lower 37.3% of WS 904 lay within the treated area (Fig. 1). The control, WS 901, was also perennial in nature. Mean daily flow-weighted streamflow volumes were computed by standard methods at USDA Forest Service's Coweeta Hydrologic Laboratory (Hibbert and Cunningham, 1967). Daily streamflow volumes were multiplied by mean daily stream picloram concentrations and summed for April 1981 through January 1982 to estimate total picloram offsite movement from WS 904.

A downstream sampling site (Manning site, Fig. 1) was instrumented with a discrete, automatic water sampler (Manning S4040T). Continuous flow measurements were not made at this site, but periodic flow estimations were made by using stream surface velocity and cross-sectional area. A rain-gauge station was installed on a ridge between WS 902 and WS 903. One standard storage gauge and a weighing-bucket-type recording rain gauge were installed at the same time as the H-flumes.

Watershed 902 was also instrumented with tension-cup porous lysimeters (Hansen and Harris, 1975). Four lysimeters were installed 0.45 m deep at each of three topographic positions (ridge, midslope, and toe). Three additional lysimeters were buried 1.0 m deep in the ephemeral channel to sample interflow moving beneath the surface H-flume during nonstorm conditions.

Herbicide Treatment

The area outlined in Fig. 1 (dashed lines) was burned in late 1980 to remove kudzu litter from the soil surface. Picloram pellets (10% a.i.) were applied by air on 7 Apr. 1981 at the standard labeled rate of 56 kg ha^{-1}. A helicopter equipped with saddle tanks spread the herbicide pellets in a series of north-south and east-west patterns. A streamside herbicide exclusion zone was delineated along the main perennial drainage area up through WS 904. However, picloram pellets were inadvertently dropped in this zone because of difficulties in identifying the stream area from the air.

Sample Collection

Mineral soil samples were collected 25, 30, 46, 77, 102, 158, 241, and 366 d following the herbicide application (11, 16, 32, 63, 88, 114, 227, and 352 d after first rain activated pellets). Ridge, mid-, and toe slope positions were sampled at depths of 0 to 15, 15 to 30, and 30 to 45 cm. Along each slope position 25 to 30 cores (19-mm diam.) were taken at random locations and composited by depth for each of three watersheds on each sample date. Composited samples were thoroughly mixed and subsampled for analysis.

Soil solution samples were collected at 3- to 5-d intervals for the first 260 d after herbicide application. Tension-cup porous lysimeters were initially adjusted to 0.02MPa, and readjusted to that value following each sample collection.

Streamflow samples were collected at 4-h intervals and composited daily at the Manning site, and daily from the flow proportional sampler at WS 904 for the first 120 d after application of picloram. Additional samples were composited biweekly for the next 180 d. Samples were also collected 330, 360, and 480 d after application. The ephemeral watersheds (WS 902 and WS 903) produced samples on only 10 d during the first 60 d of monitoring.

All soil and water samples were transported immediately after collection to USDA Forest Service's analytical laboratory at Auburn, AL, where they were stored frozen until analyzed.

Analytical Methods

Picloram residues in soil and water samples were determined by reversed-phase liquid chromatography (Wells et al., 1984). The sample cleanup procedure involved combinations of liquid-liquid partitioning of acidified extracts with ether, and adsorption trapping on basic alumina (soils) or reversed-phase sorbents (soils and water). The concentrated extracts were analyzed by reversed-phase liquid chromatography with a Waters Associates Model 440 liquid chromatograph equipped with a Waters WISP 710B automatic sample feed and a Perkin-Elmer Sigma 10 data acquisition system. Picloram determination was based on ultraviolet absorption by the underivatized free acid. Detection limits were I mg m^{-3} for streamwater, 2 mg m^{-3} for soil solution samples, and 0.01 mg kg^{-1} for soil samples. Recovery of picloram from fortified control samples was 92% ± 7. 1 for all water samples and 61.8% ± 1 1. I for soil. All concentration values reported in this paper are raw values that have not been corrected for recovery.

RESULTS AND DISCUSSION

Mineral Soil

Picloram was released into the mineral soil by rainfall 14 d after the herbicide application. Eleven days later, residues in the upper 15 cm ranged from $96 to 2.25 mg kg^{-1} (Table 1). Picloram concentrations decreased with sample depth throughout the study (Tables 2 and 3) and dropped to about 10% of their initial values in surface soil samples 1 yr after application.

Picloram residues were highly variable in mineral soil across the range of depths, sampling dates, and slope positions. Much of this variability may have been due to the inherently uneven distribution associated with applications of pelleted formulations. Coefficient of variation of means by depth for the three watersheds sampled ranged from 3 to 124% and averaged 54%. Mineral soil collected from the toe slope position produced the most regular time-concentration trend (Fig. 2). Peak picloram concentrations were delayed in time going from ridge positions to the toe of the slope (Table 1). Herbicide residues were at their maximum on ridge sites 11 d after the first rain (2.25 mg kg^{-1}), on midslope sites 16 d after the event (2.11 mg kg^{-1}), and on toe-slope positions 32 d after first rainfall (2.58 mg kg^{-1}). This trend indicates that some downslope migration of picloram residues may have occurred in the 0- to 15-cm soil layer, but the differences are not statistically significant. Data from samples collected at depths of 15 to 30 cm show a similar but less pronounced trend (Table 2). A similar pattern in concentrations of herbicide residue was observed with hexazinone in a sandy loam (Typic Hapludult) soil (Neary et al., 1983).

Table 1. Concentrations of picloram in a Typic Kanhapludult soil at the 0- to 15-cm depth 25 to 366 d after application, Tuskegee National Forest, Alabama.

Days since:		Slope position†		
Application	First rain	Ridge	Mid	Toe
		mg kg^{-1}		
25	11	2.25 ± 0.08‡	1.39 ± 0.77	0.96 ± 0.49
30	16	1.62 ± 0.84	2.11 ± 1.30	0.81 ± 0.19
46	32	2.10 ± 1.31	1.74 ± 1.19	2.58 ± 1.96
77	63	0.42 ± 0.04	0.68 ± 0.25	0.61 ± 0.30
102	88	1.67 ± 1.13	0.24 ± 0.16	0.62 ± 0.51
158	114	0.46 ± 0.26	0.73 ± 0.16	0.60 ± 0.34
241	227	0.62 ± 0.19	0.73 ± 0.45	0.45 ± 0.56
366	352	0.29 ± 0.16	0.16 ± 0.03	0.13 ± 0.09

† Values reported are means for three watersheds.
‡ Mean ± standard deviation.

Picloram dissipation from treated soil is presented for the toe slope position in Figure 2. Half-life ($T_{1/2}$, the time for dissipation of half of the maximum observed concentration) in soil was calculated from simple linear regression of the log of soil concentration (Dependent variable) vs. time (independent variable). Regression correlation coefficients (R) ranged from

Table 2. Concentrations of picloram in mineral soil at the 15- to 30-cm depth 25 to 366 d after application, Tuskegee National Forest, Alabama.

Days since:		Slope position†		
Application	First rain	Ridge	Mid	Toe
		mg kg^{-1}		
25	11	0.48 ± 0.30‡	0.25 ± 0.15	0.25 ± 0.09
30	16	0.57 ± 0.41	0.90 ± 0.69	0.16 ± 0.04
46	32	0.44 ± 0.18	0.50 ± 0.46	1.35 ± 1.41
77	63	0.50 ± 0.33	0.25 ± 0.06	0.32 ± 0.07
102	88	0.49 ± 0.29	0.36 ± 0.12	0.41 ± 0.19
158	114	0.20 ± 0.04	0.32 ± 0.13	0.43 ± 0.13
241	227	0.19 ± 0.16	0.11 ± 0.06	0.14 ± 0.11
366	352	0.09 ± 0.10	0.07 ± 0.04	0.04 ± 0.02

† Values reported are means for three watersheds.
‡ Mean ± standard deviation.

Table 3. Concentrations of picloram in mineral soil at the 30- to 45-cm depth 25 to 366 d after application, Tuskegee National Forest, Alabama.

Days since:		Slope position‡		
Application	First rain	Ridge	Mid	Toe
		mg kg^{-1}		
25	11	0.16 ± 0.05‡	0.18 ± 0.07	0.10 ± 0.07
30	16	0.10 ± 0.04	0.21 ± 0.19	0.05 ± 0.01
46	32	0.34 ± 0.07	0.16 ± 0.12	0.46 ± 0.39
77	63	0.25 ± 0.01	0.20 ± 0.06	0.19 ± 0.13
102	88	0.33 ± 0.21	0.32 ± 0.08	0.25 ± 0.09
158	114	0.15 ± 0.05	0.20 ± 0.11	0.17 ± 0.09
241	227	0.14 ± 0.05	0.14 ± 0.08	0.25 ± 0.22
366	352	0.07 ± 0.07	0.04 ± 0.03	0.04 ± 0.05

† Values reported are means for three watersheds.
‡ Mean ± standard deviation.

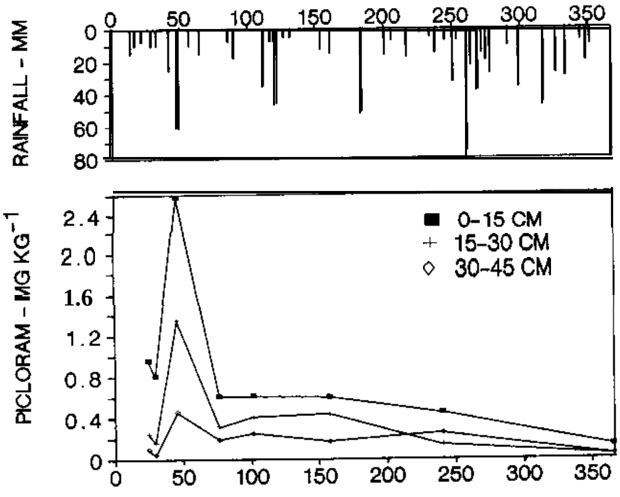

Fig. 2. Mean concentrations (three watersheds) of picloram in 15-cm deep soil increments at the toe slope position in a loamy sand (Typic Kanhapludult) following application of picloram for control of kudzu.

0.64 to 0.86. All calculations were based on the 0- to 15-cm minerals soil samples. Half lives ranged from 50 d for WS 904 to 111 d for WS 902. The variability is probably due to the highly eroded character and more xeric condition of WS 902 relative to WS 904. The more eroded nature of WS 902 was evidenced by lower organic matter content and probably decreased microbial activity. Also, there was no perennial streamflow in this watershed. WS 903 was intermediate with a $T_{1/2}$ of 66 d. These observed half-life values are well within the range of previously reported values (NRCC, 1976; USDA, 1984) and reflect the dependence of soil persistence on site conditions and soil characteristics.

Soil Solution

Picloram residues in soil solution were characterized by a high degree of variability, relatively low concentrations, and very long persistence. During the 10 to 18 wk after treatment, 7 of the 15 lysimeters did not contain any soil solution! but overall only three lysimeters did not contain soil solution sample on at least half of the 91 sampling events in this study. Four of the 15 lysimeters installed on the ridge, midslope, toe slope, and channel positions consistently produced samples with detectable picloram concentrations. Residues in these lysimeters generally persisted throughout the 390-d monitoring period. The remaining lysimeters periodically contained picloram residues. Picloram concentrations in the lysimeters that consistently contained soil solution samples were generally <400 mg m^{-3}. The maximum concentration observed in soil solution samples from a single lysimeter (1830 mg m^{-3}) occurred in the ephemeral channel lysimeters 33 d after treatment (Fig. 3).

The concentration of picloram in soil solution along the ridge was quite low during the first 275 d of monitoring. Only four samples from this time period contained quantifiable picloram residues. The highest of these (33 mg m^{-3}) occurred 54 d after treatment and coincided with the second largest storm event in the study. Heavier rainfall between 275 and 392 d after application produced more samples with detectable picloram residues (<130 mg m^{-3}). By the end of the sampling period, concentrations were close to the nondetectable level (< 1 mg m^{-3}) for two of the four lysimeters at this position, but remained in the 20 to 60 mg m^{-3} range for the remaining two lysimeters.

At the midslope position, picloram residues were frequently detected in soil solution (Fig. 4). Mean concentrations were usually in the range of 50 to 200 mg m^{-3}. One of four lysimeters accounted for 34% of all samples collected for this location, and it was also responsible for 95% of all soil solution samples containing quantifiable residues of picloram at midslope. This lysimeter, which contained the sample having the maximum observed midslope picloram concentration of 450 mg m^{-3}, may have been placed in a spot that had received an abnormal amount of picloram pellets. The remaining three lysimeters contained only three samples with quantifiable residues (>0.01 mg kg^{-1}), but contained several samples with trace residues. The second major pulse of rain, about 50 d after herbicide application, produced a distinctive flux in picloram residues, and subsequent large storm events resulted in similar fluxes, except that picloram concentrations increased slightly with these events. Concentrations at the end of the monitoring period, some 390 d after application, showed a slight declining trend.

Soil solution collected at the toe of the slope was mainly free of picloram residues until the sixth major rainy period, about 265 d after application, and followed the pattern of the ridge lysimeters. A pulse of picloram appearing in samples from three of four lysimeters raised the mean soil solution concentration to 49 mg m^{-3} (SD, 94) 277 d after treatment. Picloram concentrations declined steadily thereafter but remained detectable for the next 100 d. The maximum concentration in one lysimeter sample was 191 mg

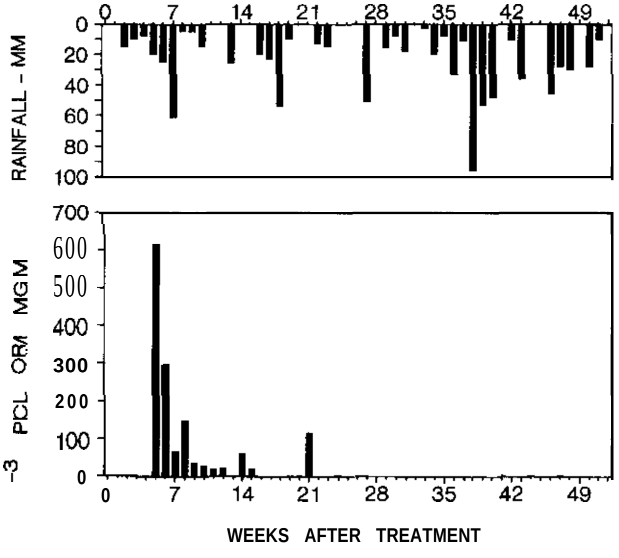

Fig. 3. Mean concentrations of picloram in soil solution sampled with three porous cup lysimeters 1 m deep under the ephemeral channel of WS 902.

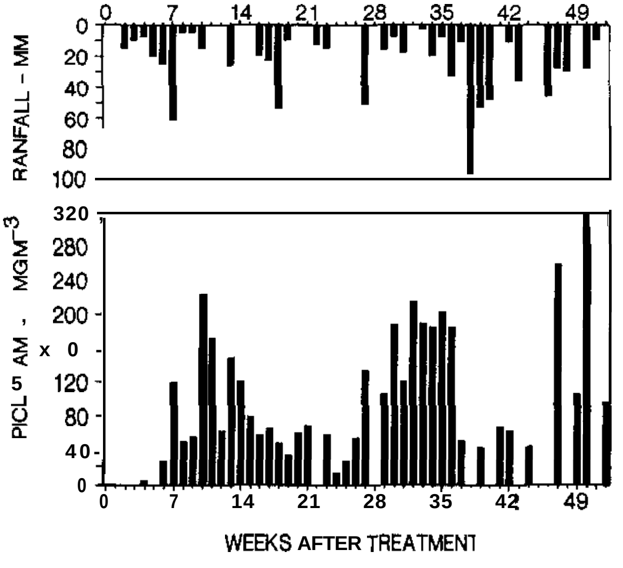

Fig. 4. Mean concentrations of picloram in soil solution sampled with four porous cup lysimeters at midslope position from the 45-cm depth.

m^{-3} 277 d after treatment. Mean concentrations did not approach the levels in samples from the lysimeters at midslope. The lower picloram concentration in soil solution at the toe-slope positions was probably due to the greater adsorptive capacity of the more colluvial soil there.

Ephemeral **Channel**

Water samples from the saturated zone 1 m below the ephemeral channel of WS 902 contained significant amounts of picloram during the first 100 d after application (Fig. 3). The mean weekly concentration peaked at 615 ± 1053 mg m^{-3} 33 d after treatment and coincided with the maximum concentration observed in any single lysimeter (1830 mg m^{-3}). Picloram levels generally declined thereafter. Few samples collected after Day 100 from this saturated interflow zone contained any detectable picloram residues, and none exceeded 20 mg m^{-3}. In addition, though all lysimeters in this area contained samples with quantifiable picloram residues, the lysimeter that had given samples containing the highest pilcoram concentrations ceased to produce any water sample 108 d after treatment. Although mineral soil samples at the 30- to 45-cm depth still contained appreciable amounts of picloram (0.04 - 0.29 mg kg^{-1}) and some soil solution samples contained 50 to 300 mg m^{-3} of this herbicide, its movement in saturated subsurface flow had apparently ceased (Fig. 2, 3, and 4). Inputs to the perennial stream from subsurface flow were greatly reduced after about 140 d (Fig. 5).

The extremely high variability of picloram concentration in soil solution in this study makes it difficult to interpret the data. Undoubtedly, the high variability in pellet distribution resulting from aerial application plays a role in the observed data, but spatial distribution alone cannot satisfactorily explain the high midslope concentrations relative to the low ridge and toe slope concentrations. Also, it seems that variability resulting from unequal spatial distribution would be reduced where confluence of subsurface flow occurred, as would be expected for the lysimeters positioned 1 m beneath the ephemeral channel. However, in this study the greatest observed variability was in the channel lysimeters. Lysimeter data from this study clearly indicate that vertical herbicide movement through the soil profile is extremely variable and that a very large number of these tension-cup soil solution samplers would be required to provide useful information on that movement.

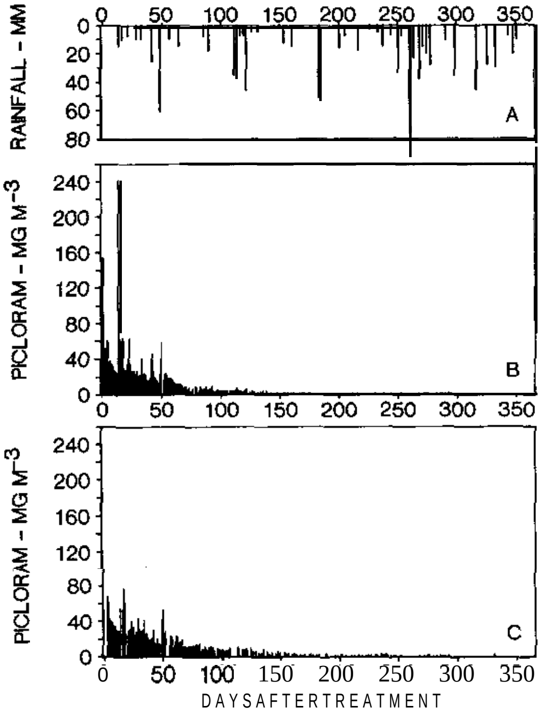

Fig. 5. Concentrations of picloram in streamflow in WS 904 (*B*), at the Manning site downstream (*C*), and daily precipitation (A) associated with the observed movement in a tributary of Uphapee Creek, Tuskegee National Forest, Alabama.

Streamflow

Watershed 904 was the only watershed within the picloram treatment area that maintained perennial flow during the study period (Fig. 1). Although only the lower one-third of this watershed was treated, significant concentrations of picloram were initially observed in streamflow. During the aerial application, some picloram pellets fell above the H-flume gauging and monitoring sites. Picloram concentrations rose immediately to 50 mg m^{-3} and eventually to 150 mg m^{-3} after the herbicide application (Fig. 5B). Some instantaneously higher values may have occurred during the aerial operation, but were not observed because manual sampling did not start until several hours after treatment.

The first rainfall event, 14 d after the herbicide application, produced the peak concentration (241 mg m^{-3}) (Fig. 5B). Picloram concentrations declined through the first major rainy period (around Day 50) and continued to drop until streamflow residues were just barely detectable (<2 mg m^{-3}) after Day 140. Concentrations in streamflow through Day 50 were high enough to kill pine seedlings if the stream water had been used for irrigation (Wu et al., 1971). In fact, picloram levels in streamflow throughout the first 100 d were high enough $>$ 10 mg m^{-3}) to kill most agronomic crop seedlings if this water had been used for irrigation (Bovey and Scifres, 1971).

Table 4. Monthly picloram runoff loss from WS 904, April 1981 through January 1982.

Month	Picloram mass lost, grams	Percent of total loss
April	162.50	56.9
May	79.68	27.9
June	21.58	7.6
July	10.66	3.7
August	4.61	1.6
September	1.36	0.5
October	0.52	0.2
November	0.65	0.2
December	1.35	0.5
January	2.60‡	0.9
Total	285.51	100.0

† Picloram loss (%) = (285.51 g × 100) / 14.5 × 10^3 g of picloram applied to treated part of WS 904.

‡ Last half of month estimated due to lack of continuous flow data.

Picloram concentrations observed in streamflow from WS 904 were not as high as that reported in the literature (2170 mg m^{-3}) on grassland watersheds (Trichell et al., 1968), but they do represent high values for forested conditions (Neary et al., 1985; Norris, 1981b). Although the long duration of picloram residues in streamflow did not include a single storm event in the category that Wauchope (1978) classed as having a catastrophic pesticide loss (>2% loss), the total amount of picloram that moved off the site in streamflow over the monitoring period exceeded 2% (Table 4). Nearly 57% of this loss occurred during the month of application (first three storms), and an additional 28% of the total loss occurred in May 1981. The total amount of picloram lost from this Upper Coastal Plain watershed represents more than six times the amount lost from watersheds studied in the Pacific Northwest (Norris, 1981b; Norris et al., 1982). Even excluding losses from direct input into the WS 904 stream, the picloram loss in streamflow would approach 1%, or three times that measured in the Pacific Northwest. The loss from WS 904 (2%) is similar to picloram loss (3.12%) reported in the Appalachian Mountains (Neary et al., 1985).

Picloram was detected in very low quantities (<2 mg m^{-3}) in streamflow from WS 904 from about Day 140 on. This includes the largest rainy period, around Day 262. The small amounts of picloram in soil solution during this period (Fig. 4) were diluted by streamflow from the untreated upper two-thirds of WS 904, but picloram residues did not totally disappear from stormflow.

Residues of picloram detected in the stream flowing from WS 904 probably did not have any impact on the aquatic ecosystem downstream. Picloram does not accumulate in aquatic invertebrates (Hardy, 1966), and measured peak concentrations were <25% of the LC_{50} for the most sensitive vertebrates and invertebrates. Also, most aquatic primary producers can tolerate picloram concentrations well in excess of the 1.0 g m^{-3} level (Elder et al., 1970). Other possible downstream impacts include damage to crops receiving irrigated stream water or to riparian tree species. Some crop species are damaged when the concentration of picloram in their growth medium exceeds 140 mg m^{-3} (Baur et al., 1972). However, damage to crops by irrigation from this site is unlikely. Stream concentrations at the Manning site were diluted by additional inputs from the large watershed subtending the Manning site, so that the high concentrations observed at WS904 were not detected (Fig. 5C). Additional dilution by the much larger watershed drained by Uphapee Creek at the point of input from the treated site would greatly dilute the observed stream concentrations of picloram to undetectable levels before the stream could become large enough to support irrigation. Mortality of several large loblolly pine trees (DBH >60 cm) and saplings of deciduous magnolia (*Magnolia* sp.) was observed along the stream at the Manning sampler, but tissue analysis to confirm the presence of picloram in those plants was not conducted.

Watersheds WS 902 and WS 903 produced very little stormflow. Thus, the contribution of surface runoff from ephemeral watersheds to picloram off-site movement was minor. Apparently, leaching through the sandy soils and direct inputs into the perennial stream system were the major sources of picloram off-site movement.

Downstream picloram concentrations were evaluated by sampling at a point halfway to Uphapee Creek (Manning site, Fig. 1). The objective of sampling at this point was to determine how much dilution was occurring in a watershed about five times larger than ws 904.

Picloram levels at this downstream sampling point reached a maximum of only 77 mg m^{-3} during the first rainfall, dropped steadily to below 10 mg m^{-3} after 90 d, and then declined to below 2 mg m^{-3} by 200 d after application (Fig. 5C). The streamflow concentration pattern generally followed that of WS 904, especially during the long droughty periods at the study site. However, during the first major storm event at 14 d after treatment, stream concentrations at the Manning site were about 25% of the concentrations observed on WS 904. At the time of this storm, soils were moist and considerable runoff was produced. Storms subsequent to the onset of the drought (several periods of 25 to 30 d without measurable precipitation) produced little runoff. Two samples collected during the second summer after application and following a spot treatment for resprouting kudzu showed slight increases in picloram concentration. Monitoring should have been carried on for at least another year. Concentrations in these last two samples (20 - 30 mg m^{-3}) were low.

CONCLUSIONS

Aerial application of granular picloram herbicide resulted in off-site movement in streamflow and sub surface leaching. The largest source of picloram in streamflow was storm runoff. Although picloram concentrations were not high enough to impact aquatic primary producers, invertebrates, or fish, they were at phytotoxic levels for some agronomic crops and probably for some sensitive nontarget woody riparian species. Use of streamflow from the treated watershed for irrigation during a period of up to 200 d after application could have produced nontarget impacts, but such use did not occur because the stream was not large enough to support irrigation and because of the ownership of adequate buffer area surrounding the treated area. Picloram is a restricted-use herbicide because of its high toxicity to agronomic crops. Because a suitable, easily identifiable streamside buffer zone was lacking, picloram was accidentally dropped into a small perennial stream and onto the streambank. Direct input and storm runoff resulted in concentrations higher than in most other monitored forest applications. Thus, use of alternative chemicals should be considered near stream systems that have poorly defined buffers.

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Productivity of Clay Tailings from Phosphate Mining: I. Biomass Crops

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ABSTRACT

Phosphate mining in Florida yields waste products of phosphafic clay and quartz sand tailings, each making up about one-third of the original matrix (PO, ore, sand, and clay). Phosphatic clay ponds typically occupy about 50% of the mined sites and normally require 10 to 15 yr before 40 to 50% solids are obtained. These clays contain no phytotoxic materials and are high in most plant nutrients. When surface water has disappeared, these clays are classified as clayey Haplaquents. A split-plot field experiment was conducted to study biomass yield, quality, plant nutrient concentrations, changes in soil nutrients, and ^{226}Ra. Seven biomass crops-(i) elephantgrass (*Pennisetum purpureum* L. 'PI 300086'), (ii) leucaena [*Leucaena leucocephala* (Lam.) De Wet], (iii) alemangrass [*Echinochloa polystachya* (H.B.K) Hitchc], (iv) erianthus [*Erianthus arundinaceum* (Retz) Jesw 'IK 76-63'], (v) desmodium (*Desmodium cinerascens* A. Gray), (vi) sweet sorghum [*Sorghum bicolor* (L.) Moench 'USDA M 81E'], and (vii) forage sorghum [*Sorghum bicolor* (L.) Moench 'Pioneer 931']—were grown on the phosphatic clay with and without a 5-cm surface layer of quartz sand tailings. Nitrogen was the only fertilizer element applied for grass species and no fertilizer was applied for legumes during the 4-yr period. Dry biomass yield averaged over 4 yr for erianthus, leucaena, and elephantgrass averaged 139.6, 58.5, and 56.5 Mg ha^{-1} yr^{-1}, respectively. Crude protein and digestibility were low in mature, whole-plant samples except for leucaena (122.0 g kg^{-1}). Generally, all whole plants contained adequate concentrations of nutrients averaging (g kg^{-1}) P, 2.05; K, 11.5; Ca, 4.3; Mg, 2.77 and (mg kg^{-1}) Cu, 4.0; Zn, 26; Fe, 68; and Mn, 35. Mehlich-I-extractable soil nutrient concentrations changed little over the 4-yr period. Radium-226 concentration in plant tissue (0.23 pCi g^{-1}) was nearly six times higher than the concentration measured in plants from an unmined surface Spodosol (0.04 pCi g^{-1}). Data indicate that these present-day waste lands can be a valuable resource for biomass production.

PHOSPHATE MINING in Florida is accomplished using a dragline to dig a series of parallel cuts several hundred to several thousand meters in length and 60 to 100 m wide. Overburden is cast into previously mined cuts and the underlying matrix (quartz sand, phosphate pebble, and phosphatic colloidal material) is exposed. The matrix is removed and transferred to a slurry pit where large water jets (monitors) deliver 37 000 to 45 000 L water min^{-1} at a pressure of 1.45 X 10^6 Pa, which breaks the friable ore into a slurry. The slurry is screened through a steel grid to remove rocks and debris and pumped to the beneficiation plant (24). It is then processed to remove useable phosphate rock, while quartz sand and phosphatic colloidal material are collected as residual waste products and are

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