

Herbicides and the Range Ecosystem: Residues, Research, and the Role of Rangemen

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Highlight: Increasing sophistication in application techniques, herbicide chemistry, and related technology in conjunction with intensified public awareness of herbicide use on rangeland has provided the impetus for research on the fate of herbicides in the range ecosystem. The complexity of the range ecosystem in comparison to monocultural systems dictates that persons versed in range ecology and herbicide technology conduct necessary research and play a dominant role in interpretation of results. The role of the atmosphere, ecosystem surfaces, vegetation, soil, and water in herbicide transfer and dissipation from the range ecosystem are reviewed. Properly applied, herbicides applicable to range improvement programs provide excellent levels of weed and brush control without undue hazard to sensitive crops; do not endanger man, his livestock or wildlife; and, in most cases, are dissipated from the ecosystem during the growing season in which they are applied.

Herbicides have been integral parts of range improvement systems for over 25 years. However, until the late 1940's and early 1950's, most herbicide use was as individual-plant treatments; and, available herbicides were not highly selective. It would have been interesting to have observed the reactions of the first ranchers who were told, after fighting brush by hand and with heavy equipment for most of their lives, that new chemicals had been developed which, when sprayed in small quantities on the brush, would kill the trees with little or no damage to the grasses. Rapid technological advancement, especially in herbicide development and methods of application, provided the capability of rapidly treating extensive acreages with aircraft.

Brush and weed control on rangeland is basically a management problem that must be approached on an ecological basis within an economic framework. Effective herbicides are essential tools for the modern range resource manager. Herbicide use for range improvement serves as an ideal example of the increasing complexity of effectively approaching the brush problem in the Southwest when proper management, ecological requirements, and economic criteria are considered.

In the early days, the ultimate fate of herbicides after application to rangeland was a relatively small consideration, especially if the chemicals were known to be nontoxic to grazing animals. Also, most herbicide use was concentrated on large

areas much of which was privately owned. Public opinion played a minor role in the decision-making process involved in management and use of these lands. Also, most of the range improvement efforts with herbicides involved use of one class of chemicals, phenoxy herbicides, primarily 2,4-D [(2,4-dichlorophenoxy)acetic acid], 2,4,5-T [(2,4,5-trichlorophenoxy)acetic acid], and silvex [2-(2,4,5-trichlorophenoxy)propionic acid]. Herbicides and the technology associated with their use have become more sophisticated in the past 25 years; and public interest in the use and management of all natural resources has intensified. Range researchers have made an exceptional contribution to the knowledge base relative to performance of herbicides and their use in range management. However, today's rangemen, ranchers, researchers, educators, public land managers, and action-agency personnel, must also be broadly versed in the fate of herbicides after application to rangeland. Until approximately 10 years ago, most of the research dealing with the fate of herbicides was left to agronomists, plant physiologists, and others who dealt primarily with monocultural systems. However, qualified rangemen must take a more active part in conducting residue research to assure their proper role in data interpretation; and, most important, an active voice in the decision-making processes affecting herbicide use patterns on rangeland.

Technological sophistication in residue research is being directly applied to studies in the range ecosystem with herbicides. A few years ago, 0.5 to 1 part herbicide residue per million parts of air, soil, water, or vegetation was considered a sensitive lower limit of detection. Techniques have been refined such that residue levels of many herbicides are presently measured as parts per billion (Merkle et al. 1966). Methods are being developed which may ultimately make it routinely possible to detect herbicides at *parts per trillion levels!* If time relationships were compared, 1 second lapse every 11.57 days is equivalent to 1 ppm; and 1 second lapse every 31.7 years is roughly equivalent to 1 ppb. Based on weight, 1 lb of soil mixed with a 6-inch layer from 1 acre in area equals 1 part per million; and 1 lb of soil mixed in the same 6-inch layer but from 1,000 acres is roughly equivalent to 1 ppb. Obviously, such sensitivity allows detailed monitoring of the fate of herbicides in the environment. However, the biological significance of these almost infinitely small quantities of herbicides in natural systems must be defined and common sense asserted in the decision-making process. This logic may be best offered by workers with a grasp of requisites for effective natural resource

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management who are qualified to assess the significance of given levels of herbicide residues.

The complexity of range ecosystems, especially the diversity in vegetation and soils, makes research on fate of herbicides in rangeland more complicated than in cropland. An understanding of the form and function of these natural systems is required for proper interpretation of research results leading to decisions concerning herbicide use. To reiterate, *it is critical that rangeland play an active part in conceiving, devising, conducting, and interpreting research on dissipation of herbicides from rangeland.*

Since the early 1960's, considerable research has been conducted on herbicide residues in rangeland emphasizing their longevity in various portions of the ecosystem and the interrelations of the atmosphere, vegetation, soil, and water with herbicide dissipation. The following is a summary of the residual potential of phenoxy herbicides (primarily 2,4-D and 2,4,5-T, picloram (4-amino-3,5,6-trichloropicolinic acid), and dicamba (3,6-dichloro-*o*-anisic acid) in various compartments of the range system. Although the latter two herbicides are commercially formulated in various ratios with the former two, there is no evidence that their application in mixtures influences rate of dissipation of either component. Therefore, the herbicides will be dealt with separately. Dry formulations of picloram and dicamba are available and show promise for some range uses; however, aerial application of sprays for weed and brush control are emphasized in this paper.

The spray contacts the environment immediately upon release from the spray nozzle, and must travel through the atmosphere to reach the target (undesirable vegetation). A certain portion of the chemical comes in contact with the soil and eventually with the soil solution. Consequently, water solubility of the herbicide and weather conditions, especially occurrence of precipitation following application, determine relative mobility of the herbicide in the ecosystem.

Each environmental component, atmosphere, vegetation, soil, and water, will be discussed separately. However, it is understood that the environment cannot be compartmentalized in the strictest sense; and the interactions among compartments may be of more importance than activity within a compartment (Bovey and Scifres 1971) (Fig. 1).

Atmosphere Effects

The most pronounced atmospheric effects on herbicide sprays are spray drift (displacement of airborne spray particles from the target area) and volatilization (the conversion of liquid to a gas). The action of air currents is primarily responsible for extent of spray drift as related to (1) droplet size, (2) wind direction and velocity, and (3) height above the target at which the spray is released.

Droplet size is affected by spraying pressure, type of carrier (whether oil or water), and nozzle size. In general, low spraying pressure and large nozzle orifices produce large droplets. As the spraying pressure is increased and/or nozzle orifice size decreased, the spray is broken up into progressively smaller particles increasing potential for their displacement.

As the spray droplets fall through the atmosphere, they become increasingly smaller until completely evaporated (the rate of evaporation depends on temperature, relative humidity, and carrier) or until contacting a plant or soil surface. Thus, the height above ground line at which sprays are released is extremely important in regulating extent of spray drift. Obviously, the potential for spray drift is greater from aerial than

from most ground sprayers. In general, 8 to 10 mph winds at ground level are borderline velocities for aerial application of sprays. Where susceptible crops are in close proximity to the spray operation and the air temperature is 85°F or higher, aerial spraying probably should not be considered, especially in wind velocities of 8 mph or greater. The definite upper limits for spraying are air temperature of 90°F and a wind speed of 10 mph, *especially when applying herbicides within a mile of highly susceptible crops such as cotton, soybeans, fruit crops, and garden vegetables.* Also, it is highly desirable that the relative humidity be at least 30% during spraying to promote effective foliar absorption.

The tendency of herbicide to volatilize is directly related to its vapor pressure. Vapor pressure is the pressure exerted when a solid or liquid is in equilibrium with its own vapor and is a function of the substance and of the temperature. Herbicide vapors may escape the target area and damage susceptible crops or simply reduce herbicide effectiveness by reducing amount of chemical at the target area. Formulation, the chemical form for dispensing the herbicide, strongly affects potential for volatility (Marth and Mitchell 1949; Que Hee and Sutherland 1974). Salt formulations, for example the potassium, dimethylamine, and triethanolamine salts, of herbicides have relatively little tendency to volatilize, whereas certain esters are prone to volatilization. Drift potential (vapor + physical) of the butyl ester of 2,4-D was found to be eight times greater than the dimethylamine salt (Grover et al. 1972). Tendency of esters to volatilize is directly related to length of the side chain. For example, two commonly used esters of 2,4-D, the isopropyl and the butyl, are

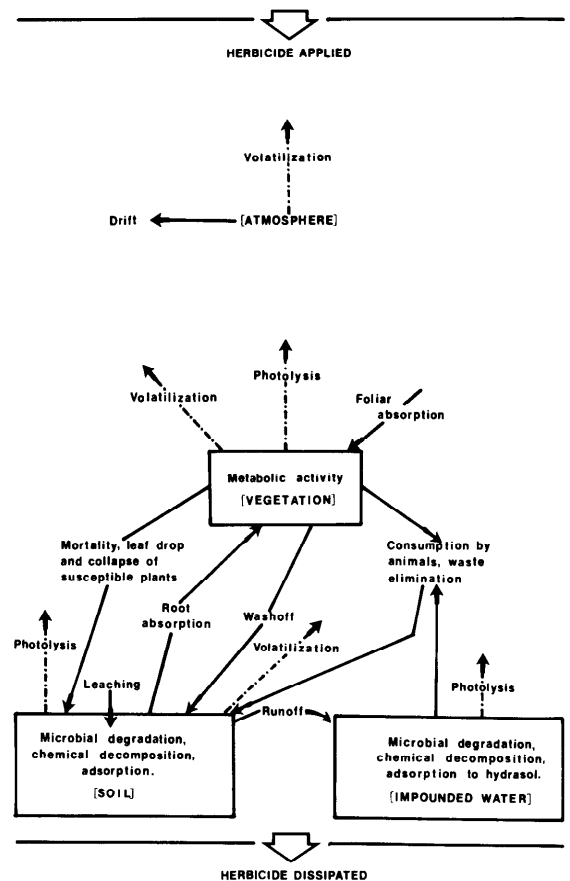


Fig. 1. Documented modes of herbicide dissipation from range ecosystem and mechanisms of transfer of residues among atmospheric, vegetational, edaphic, and aquatic components.

short chain esters and in the "high volatility" category. Examples of "low volatile" esters are the propylene glycol butyl esters and the butoxyethanol ester.

Specific chemical activity also greatly affects extent of herbicide damage from volatilization and may over-ride the influence of formulation. Although salts do not volatilize readily, vapors from the potassium salt of picloram were more toxic to broadleaved plants than those from the propylene glycol butyl ether esters of 2,4-D (Genter 1964). This, presumably, is due to the extremely strong growth regulating properties of picloram. Smaller amounts of picloram were volatilized than the 2,4-D ester but did more damage than the latter to the susceptible crop.

The significance of loss of herbicides to the atmosphere was demonstrated by Adams (1964). They obtained air samples near Pullman, Washington, over a 106-day period (May–August) and estimated 2,4-D content. The samples contained detectable and identifiable 2,4-D esters on more than 90% of the 106 days sampled.

Loss of Herbicides from Surfaces

Once the herbicide has traveled through the atmosphere, it must come into contact with, and remain for some time on, surfaces in the ecosystem. These surfaces are most usually afforded by mulch, plants, soils, or water. Animals in the ecosystem at the time of spraying must also be considered as affording environmental surfaces but probably an insignificant amount. Herbicides on plant surfaces may be absorbed by the foliage, consumed by animals, volatilized, washed onto the soil surface, or decomposed by light (photolysis) (Fig. 1). Residue on soil surfaces may be leached into the soil profile. The probability and extent of leaching depends on formulation (water solubility) and timeliness of rainfall after herbicide application.

Phenoxy herbicides and dicamba evidently are not as rapidly photodecomposed as picloram. Photolysis of picloram by sunlight is slower than under continuous ultraviolet light but photodecomposition is considered a significant route of picloram loss from natural systems (Hall et al. 1968). Ester formulations are more susceptible to photolysis than salt formulations of picloram (Bovey et al. 1970). Also, salt formulations, being highly water soluble, are more likely to be leached into the soil and protected from light than are esters (Bovey et al. 1969).

Herbicide Persistence in Plants

Herbicides absorbed by plants persist for varying lengths of time depending on plant species and weather. There is some concern relative to persistence of herbicides in forage and possible transfer through grazing animals to man. The broad-scale use of phenoxy herbicides has resulted in more research on these compounds than on other materials. Most 2,4-D esters are converted by the plants to the acid form within 0.5 hour after application. Milk from cows grazing sprayed pastures may contain small amounts (less than 1 ppm) 2,4-D for a few days after spraying (Klingman et al. 1966). By 4 or 5 days after spraying, residues in milk are usually not detectable. Persistence of 2,4-D, 2,4,5-T, and dicamba has been compared in many grasses including silver bluestem (*Bothriochloa saccharoides* (Swartz.) Rydb.), little bluestem (*Schizachyrium scoparium* (Michx.) Nash), dallisgrass (*Paspalum dilatatum* Poir.), and sideoats grama (*Bouteloua curtipendula* (Michx.) Torr) (Morton et al. 1967). Half-lives of the herbicides generally was 2.5 to 3 weeks. In other studies, 98% of the 2,4,5-T

applied was dissipated from native grass after 6 weeks (Bovey and Baur 1971). Rainfall is evidently important in accelerating dissipation of the herbicides from dry forages and metabolic activity from renewed growth in living grasses.

Rates of picloram loss from grasses, primarily buffalograss (*Buchloe dactyloides* (Nutt.) Engelm.), of northwest Texas rangeland following application of 0.25 lb/acre was measured at 2.5 to 3%/day for 30 days (Scifres et al. 1971). At higher rates (0.5 to 2 lb/acre) picloram may persist in grass tissues for 8 to 16 weeks (Getzendaner et al. 1969). In general, picloram is more persistent in forage than 2,4-D, 2,4,5-T, or dicamba.

Little research has been conducted on herbicide persistence in woody plants. Leaf drop following herbicide application is a mechanism of transfer to the soil surface (Scifres et al. 1971); but much of the herbicide intercepted by woody plants is moved into the wood and dissipated (Baur et al. 1969).

Surface Movement of Herbicides

After contacting plant and soil surfaces, herbicides are susceptible, depending on water solubility, to movement into the soil profile or, theoretically, across the soil surface to impounded water supplies. Highly water-soluble formulations, such as amines, are usually moved into the soil with first moisture contact (Barnett et al. 1967) rather than being washed off unless (1) a high-intensity storm occurs shortly after application (especially of a high herbicide rate); (2) the surface is extremely heavy textured and/or compacted; (3) the site supports a very low cover of vegetation; and (4) slope is excessive. The less water-soluble ester formulations will be washed off the soil surface in greater quantities than amines (Barnett et al. 1967). Application of high rates of pellet formulations may increase washoff potential as compared to sprays (Davis and Ingebo 1973).

Experiments in northwest Texas indicated that rainfall must occur almost immediately after application of picloram formulated as the triethanolamine salts to wash appreciable quantities from rangeland (Scifres et al. 1970). Heavy rainfall the first few days following application of the herbicide resulted in 17 ppb detectable residue of picloram in surface runoff. Rainfall 20 or 30 days after application 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.

Extent of vegetation cover and soil surface characteristics are also important to potential runoff of herbicides. Loss of picloram was greater from sod than from fallow plots; and, the maximum loss obtained with rainfall within 24 hours after application was 5.5% for picloram, dicamba, or 2,4,5-T (Trichell et al. 1968). The average herbicide loss was approximately 3%. The probability of runoff of significant quantities of herbicide under normal usage patterns for range improvement is relatively low (Baur et al. 1972).

Movement of Herbicides through Soils

Herbicide not dissipated from the environmental surfaces may be moved into the soil by rainfall (Fig. 1). Movement into the soil profile is more likely to occur than complete degradation on the soil surface. The rate of leaching depends on (1) soil permeability, (2) herbicide solubility (regulated to a large extent by formulation), and (3) relative affinity of the herbicide for the soil colloid and/or organic matter fraction.

Picloram in the salt or amine form is highly water soluble and can be expected to move with the wetting front in soils (Baur et

al. 1972; Hamaker et al. 1966; Scifres et al. 1969). The degree and rate of movement are dictated by characteristics of the vegetation and soil and the rate of picloram applied. In general, when a low rate (0.5 lb/acre or less) is applied to rangeland, especially those with clay soils, downward movement is much less than where higher rates are applied to highly permeable, sandy soils (Scifres et al. 1969). The degree and rate of movement are dictated by characteristics of the vegetation and soil and the rate of picloram applied. In general, when a low rate (0.5 lb/acre or less) is applied to rangeland, especially land with clay soils, downward movement is much less than where higher rates are applied to highly permeable, sandy soils (Scifres et al. 1969). However, even in sandy loams to fine sands, most picloram residues remain in the surface 2 to 3 feet of soil (Scifres et al. 1971; Scifres et al. 1976).

Most phenoxy herbicides are rapidly absorbed on soils high in organic matter which reduces movement through the profile. The tendency of ester formulations to leach through soil profiles is reduced by their lower water solubility. For instance, when enough water was added to Pullman silty clay loam to move the wetting front to 22 inches, an amine salt of 2,4-D was leached to 15 inches deep; and amine salts of 2,4,5-T and silvex were leached to approximately 9 inches (Wiese and Davis 1964). Esters of 2,4-D, 2,4,5-T, and silvex remained in the top 3 inches of soil. Once phenoxy herbicides are adsorbed on soils, they resist leaching and usually degrade without further vertical movement in the profile.

Subsurface lateral movement is dependent on direction and rate of soil water flow. Subsurface lateral movement, however, is apparently of lesser importance than vertical mobility of herbicides in the soil profile (Bovey et al. 1975; Scifres et al. 1971). Drainage samples were recovered from a field lysimeter for a year after treatment of a watershed with 1 lb/acre of 2,4,5-T + picloram (1:1) (Bovey et al. 1975). Picloram was detected only in small amounts, 1 to 4 ppb, in lysimeter water 2 to 9 months after application.

Persistence of Herbicides in Soils

Too often, herbicide residues in soils are considered undesirable. However, herbicides such as dicamba and picloram are readily taken up by the roots of many undesirable species. Therefore, residual activity in the soil may be beneficial by affording herbicides available for root uptake which, ultimately improves control level of some species (Bovey and Scifres 1971). Primary factors which affect length of residual activity of herbicides in the soil are susceptibility to (1) decomposition by microorganisms, (2) adsorption on the soil colloid, (3) chemical decomposition, and (4) leaching.

Microbial detoxication of herbicides is an important method of regulating persistence of many herbicides in soil (Klingman et al. 1975); and at normal rates under field conditions, there are no documented cases of herbicides significantly reducing microbial growth. Microbial decomposition of herbicides is affected by weather and soil conditions (notably soil temperature, moisture content, and soil reaction). Any factor that restricts growth of microbial populations consequently retards the rate of herbicide breakdown. Cool, dry, poorly aerated soils retain herbicide longer than warm, moist, well aerated soils (Friesen 1965; Hahn et al. 1969; Hamaker et al. 1967; Grover 1970). The generalized optimum temperature for herbicide degradation by microbes is 80 to 90°F with soil moisture at 50 to 100% of field capacity. Effect of soil reaction depends on the particular herbicides and microbes involved (Corbin and Upchurch 1967).

There are some indications that microbial populations "adapt" to certain herbicides and utilize the carbon as an energy source. This has been substantiated by growth curves, the "adaptive" decomposition pattern, of microbial populations in treated soils. The "adaptive" decomposition pattern is composed of three distinct phases—a lag phase, a rapid decomposition phase, and a slow decomposition phase (Klingman et al. 1975). During the lag phase, a population of microbes capable of decomposing the herbicide develops. This phase is completed almost 20 times more rapidly for 2,4-D than for 2,4,5-T, accounting for the longer residual for the latter. The lag phase for 2,4-D may require 10 to 15 days. The rapid decomposition phase, reflecting activity of the increased population of microbes capable of degrading the herbicides, may be completed in a matter of hours. The slow decomposition phase lasts until depletion of the carbon source. Not all herbicides degraded by microorganisms require an "adapted" population. In these cases, there is no lag phase and degradation proceeds at a rate depending on relative availability of the herbicide to the microbial population.

Herbicides such as 2,4-D, which are highly susceptible to microbial decomposition, would be unlikely to persist into the succeeding year even at rates much higher than normally used for range improvement. Other herbicides such as picloram, which are decomposed only very slowly by microorganisms (Meikle et al. 1973; Meikle et al. 1974; Youngson et al. 1967) may persist for a year after application at rates of 1 lb/acre or more under cool, dry conditions with no detrimental effect on the microbial population (Goring et al. 1967).

Dicamba, although more persistent than phenoxy herbicides, is evidently degraded by microorganisms more rapidly than is picloram (Scifres and Allen 1973b). Dicamba is more readily adsorbed on clay than sands and dissipated more rapidly from acidic than from basic soils (Corbin and Upchurch 1967). Extent of dicamba leaching may be dependent on time from application to first rainfall (Scifres and Allen 1973b). The herbicide moves with the wetting front in soil profiles, including upward movement with subirrigation (Harris 1964). Although dicamba is more persistent than 2,4-D in soil, general degradation conditions are evidently similar for the two herbicides.

Dissipation of dicamba from soils is usually complete within a month after application of low rates (≤ 0.25 lb/acre) to grasslands and 2 to 4 months after application of moderate rates (0.5 to 1 lb/acre) (Scifres and Allen 1973b). Residues of dicamba in the soil usually occur no deeper than 3 to 4 ft following application of moderate herbicide rates. Dicamba sprays are usually applied at 0.5 to 1 lb/acre for grassland restoration. Thus, it is unlikely that residues will persist in the soil for the duration of the growing season from spring application.

Adsorption of picloram on organic matter is of more importance than affinity for clay (Hamaker et al. 1966; Grover 1971). This lack of affinity for the colloid may account for the relatively high mobility of picloram in soils.

Herbicides in Impounded Water

As previously mentioned, there is a low probability that large quantities of herbicide will be transferred by surface movement. However, some herbicide may be introduced directly into impounded water during the spray operation. Once in the water system, herbicides are degraded by the same general mechanisms as in the soil. Esters of phenoxy herbicides are hydrolyzed to the acid form as an initial step in dissipation (Bailey et al. 1970).

Microbial decomposition is an important mode of dissipation of phenoxy herbicides and dicamba from aqueous systems. Light in the presence of sediment augments the dissipation of dicamba (Scifres and Allen 1973a).

Photolysis is evidently an important mode of picloram loss from impounded water (Haas et al. 1971). Decomposition follows a concentration-dependent curve proceeding rapidly at first then slowing as picloram concentration in the water is reduced. Phenoxy herbicides may be adsorbed by the pond sediment (Bailey et al. 1970; Frank and Comes 1967); however, it is doubtful that picloram is highly adsorbed in view of resistance to adsorption in soils (Grover 1971). Relative persistence in impounded water of herbicides used for range improvement would be 2,4-D, 2,4,5-T, silvex < dicamba < picloram. Due to the low order of toxicity of these herbicides, they should not present a hazard to livestock or wildlife (Kenaga 1969; Leng 1972; Palmer and Radeleff 1969; Norris 1971; Rowe and Hymas 1954; Sears and Meehan 1971). The primary hazard might be use of water containing the herbicides for irrigation of susceptible crops (Bovey and Scifres 1971).

There is no evidence that herbicides are transferred in food chains or that they are biologically magnified (Goring et al. 1967; Hardy 1966; Mullison 1970; Rodgers and Stallings 1972). Herbicides consumed by higher animals are eliminated primarily via urinary excretion (Lisk et al. 1964).

In summary, use of herbicides for range improvement has become a progressively more sophisticated area of study in the past 25 years. The fate of herbicides in range ecosystem is a complex area of study by virtue of the complexity of the ecosystem. This area of study should be pursued by persons trained in the ecology and management of natural resources to help assure proper data interpretation and application of research results.

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