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Degradation of Herbicides in the Forest Floor

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HERBICIDES ARE USED extensively to accomplish forest and range management goals. However, the continued availability of such chemical tools depends on strong proof that they can be used with minimum impact on the quality of the environment.

When economic chemicals are applied in the forest, only part of the material reaches the intended target (Figure 1). The forest floor is a major receptor of aerially applied chemicals (19).

Herbicide adsorption, surface runoff, leaching, or volatilization from the forest floor result only in the temporary storage or redistribution of chemicals. Chemical or biological degradation is the only means by which the load of environmental pollutants can be reduced. For this reason, special attention is given to herbicide degradation, particularly in the forest floor, the initial point of chemical entry into the soil.

The research reported or summarized herein is part of a continuing study of the behavior of chemicals in the forest environment. Goals of these investigations are to determine 1) the relative persistence of different herbicides in forest floors; 2) the kinetics of degradation; and 3) the impact of various economic chemicals on the persistence of associated herbicides.

Review of the Literature

Under various conditions reported in the literature, most herbicides undergo some degree of chemical or biological degradation in soil. Herbicide degradation under laboratory conditions or in agri-

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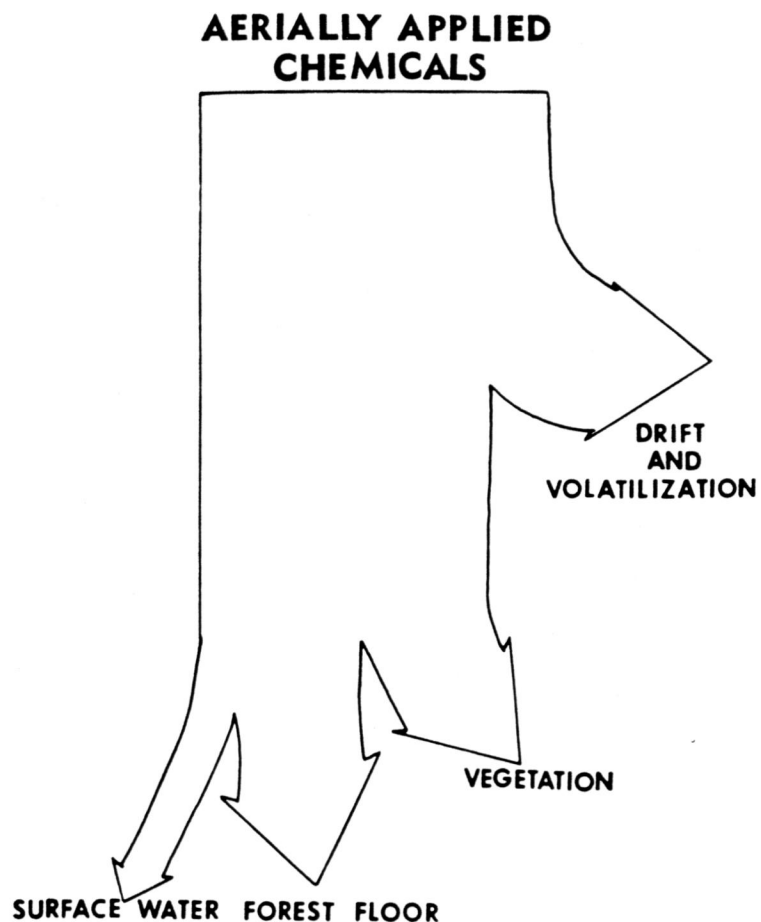


Figure 1. Distribution of aerially applied chemicals in the forest.

cultural soils is reviewed by Audus (4), Woodford and Sagar (26), and Sheets and Harris (24). Burschel (6) considered the behavior in soil of herbicides important in forestry. A report prepared for the Department of Defense contains a valuable collection of references to the persistence characteristics of herbicides intended for noncropland uses (12).

The early work of DeRose (9) and Kries (14) established that 2,4-D (2,4-dichlorophenoxyacetic acid) is degraded in the soil, prob-

ably by microbial action. In field studies, 2,4-D remained active for 6 weeks and 2,4,5-T (2,4,5-trichlorophenoxyacetic acid) lasted for 19 weeks (17). However, the kinetics of degradation of 2,4-D and 2,4,5-T are similar (2, 3).

Amitrole (3-amino-1,2,4-triazole) has been reported to lose phytotoxicity in soil with time. Freed and Furtick (10) found no amitrole residues two to six months after field application to several soil types in Oregon. Amitrole degradation has a temperature optimum of 20 to 30 C, with higher rates of inactivation occurring with high moisture availability (8).

Picloram (4-amino-3,5,6 trichloropicolinic acid) is of more recent origin than the phenoxy or amitrole herbicides, so the principles of its persistence are less well developed. Youngson *et al.* (27) found that increasing organic matter and temperature favored picloram degradation as did increasing soil moisture up to 55 percent of capacity. Hamaker, Youngson, and Goring (11) indicate that the rate of picloram degradation follows half-order kinetics.

Most studies of the behavior of herbicides in soil have been conducted with fairly pure chemicals applied alone. However, the growing intensity of forest management and the widespread use of pesticides indicate that multichemical residues will become more common. Nearly all pesticide residue monitoring programs now report finding several biologically active chemicals in many samples.

Brownbridge¹ found that soil microbes could degrade 2,4-D faster if they were first adapted to either 2,4-D or 2,4-DP [2 (2,4-dichlorophenoxy)propionic acid]. Kaufman (13) reports that the degradation of dalapon (2,2 dichloropropionic acid) was retarded in the presence of amitrole. Dalapon, on the other hand, had little effect on amitrole degradation. Nash (16) reports that two organic phosphate insecticides interact with a urea herbicide to alter patterns of phytotoxicity. These reports indicate that one pesticide may influence the action or degradation of another.

Earlier Studies of Herbicide Degradation in Forest Floor Material

Degradation of radioactive 2,4-D and 2,4,5-T

Norris (18) treated forest floor material from a red alder (*Alnus rubra* Bong.) stand with 2,4-D-1-¹⁴C or 2,4,5-T-1-¹⁴C at a rate of 2.24

¹N. Brownbridge, 1956. Ph.D. thesis, London University. Data in Audus (4).

kg/ha (2 lb/acre).² The evolution of radioactive CO_2 was measured as a function of time (Figure 2).

Both 2,4-D and 2,4,5-T were degraded, but the rate of CO_2 evolution was not the same for both herbicides. The evolution of $^{14}\text{CO}_2$ from 2,4,5-T followed zero-order kinetics up to 29 days after treatment, but evolution from 2,4-D was clearly of mixed order. The release of radioactive CO_2 cannot be quantitatively equated with herbicide degradation, however, since there is no assurance that all of the radioactive carbon removed from the herbicide molecule was released as CO_2 . Thus, the amount of degradation could be greater but not less than that indicated by these data.

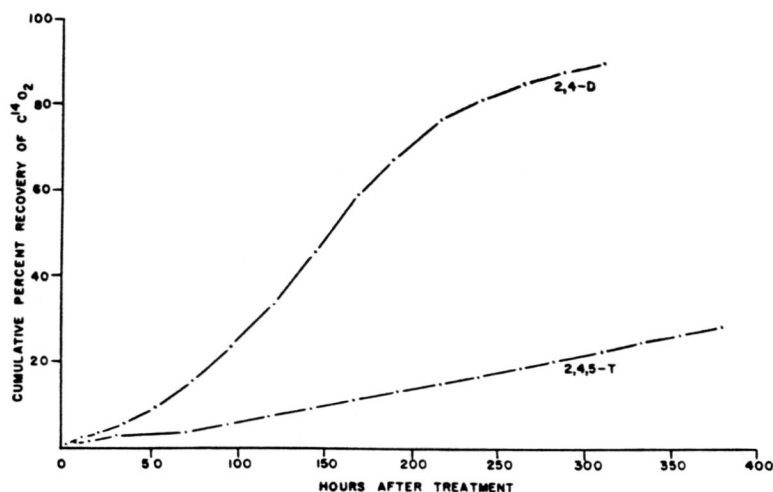


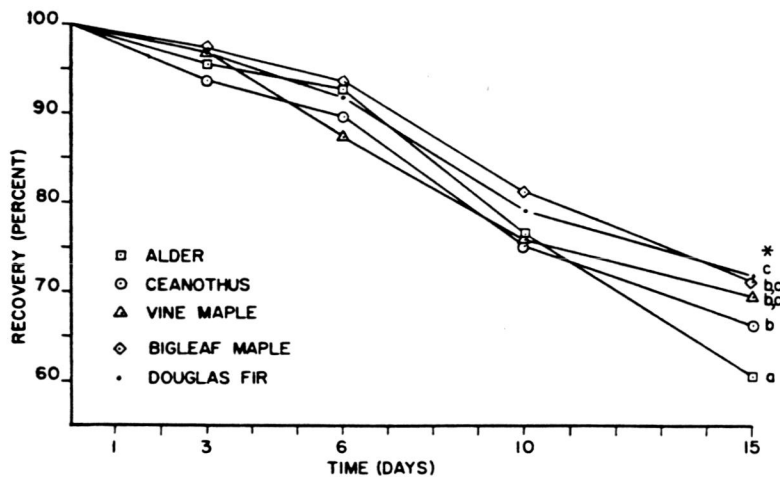
Figure 2. Liberation of $^{14}\text{CO}_2$ from red alder forest floor material treated with 2,4-D- ^{14}C or 2,4,5-T- ^{14}C .

Degradation of nonradioactive 2,4-D

Norris and Greiner (20) reported experiments in which they chemically determined the level of 2,4-D in forest floor material to obtain a direct measure of herbicide degradation. Except where otherwise indicated, 2,4-D was applied at 3.36 kg/ha (3 lb/acre) to red alder litter. These experiments are summarized below.

² All rates of application of 2,4-D, 2,4,5-T, and picloram are expressed in terms of acid equivalent.

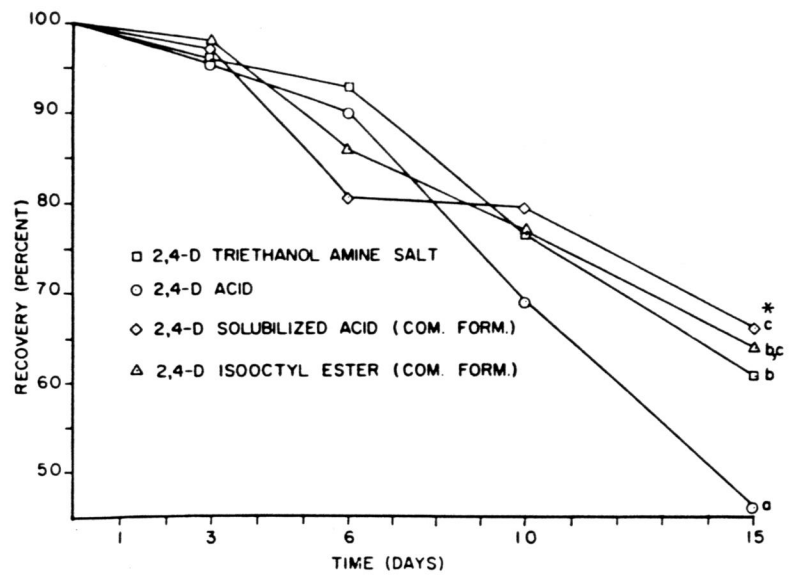
Influence of litter type. The rate of 2,4-D degradation was only slightly different in forest floor material collected beneath red alder, ceanothus (*Ceanothus velutinus* var. *laevigatus* How.), vine maple (*Acer circinatum* Pursh), bigleaf maple (*Acer macrophyllum* Pursh), and Douglas-fir (*Pseudotsuga menziesii* (Mirb.) Franco) (Figure 3). Thus, variation in the degradation rate of 2,4-D in various litter types may occur in the field, but it is more likely to be a function of microsite environment than of litter type. The general shape of the recovery curves suggests that the rate of degradation follows a mixed order of kinetics similar to that found in the first test (Figure 2).



* Recoveries at 15 days having a letter in common are not significantly different at the 5 percent level.

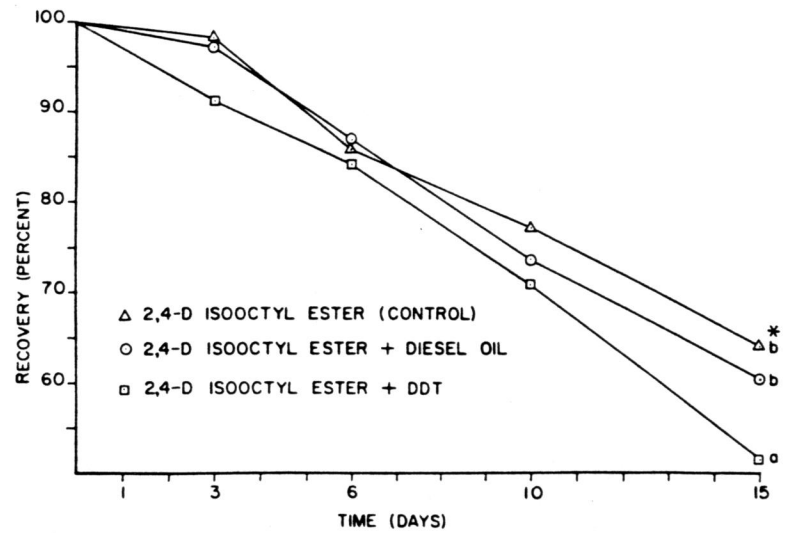
Figure 3. Recovery of 2,4-D from various types of forest floor material.

Influence of formulation. A 2,4-D acid and a triethanolamine salt formulation contained only components of high purity and were most rapidly degraded. Commercial formulations of 2,4-D isooctyl ester and solubilized acid contained the usual mixture of impurities, emulsifiers, and solvents and were less readily degraded (Figure 4). The most striking difference was between the pure acid and the solubilized acid in which the 2,4-D is in exactly the same chemical form. This retarded rate of degradation is attributed to constituents of formulation, indicating the influence that one chemical may have on the degradation



* Recoveries at 15 days having a letter in common are not significantly different at the 5 percent level.

Figure 4. Recovery of various formulations of 2,4-D from red alder forest floor material.



* Recoveries at 15 days having a letter in common are not significantly different at the 5 percent level.

Figure 5. Recovery of 2,4-D from red alder forest floor material treated with DDT or diesel oil.

of another. This point assumes large proportions when we realize that the 125 herbicides produced commercially in 1964 were offered in 8,000 different formulations.(12).

Influence of other chemicals. The insecticide DDT at 1.12 kg/ha (1 lb/acre) significantly stimulated the rate of degradation of 2,4-D isooctyl ester) when they were applied at the same time. Diesel oil at 37.4 liters/ha (4 gal/acre), commonly used as a carrier, had no effect on 2,4-D degradation (Figure 5). The persistence of the herbicide thus will not likely be adversely affected by either chemical in field applications.

Materials and Methods—Current Research

Forest floor material (L and F horizons) collected beneath red alder was coarsely chopped and preconditioned for 3 weeks in a growth chamber environment of a 15-hour day with 24 C day and 15 C night temperature. Fresh samples equivalent to 25 g oven-dry weight were placed in 110-ml waxed paper cups and returned to the growth chamber immediately after treatment with chemicals. Sprinkling maintained a moisture content averaging 54 percent (wt/wt) with a standard deviation of 7 percent over the course of the experiment.

All herbicides were highly purified and applied on a basis of surface area of the sample in 5 ml of distilled water. Picloram, 2,4-D, and 2,4,5-T were applied as the potassium salt. Amitrole was applied as the parent herbicide.

To determine the effect of insecticide residues on degradation of herbicides, the following commercially formulated insecticides were applied to forest floor samples one month before adding herbicides:

1. DDT 2 emulsive (Ortho) 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane;
2. Sevin 50W (Niagara), Carbaryl, 1-naphthyl-N-methyl carbamate; and
3. Phosphamidon 4 (Ortho) 1-Chloro-1-diethylcarbamoyl-1-propen-2-yl dimethyl phosphate.

Analytical procedures^a

2,4-D, 2,4,5-T, and picloram. Samples were homogenized and digested in 1 M KOH. After centrifugation the supernatant was acidified and liquid-liquid extracted with benzene for 2,4-D or 2,4,5-T or ether for picloram (20). Sample cleanup involved basic alumina column

^a A detailed, stepwise analytical procedure for each herbicide is available from the author on request.

chromatography as described by Bjerke *et al.* (7). After sample esterification with $\text{BF}_3\text{-CH}_3\text{OH}$, the methyl esters were extracted from the aqueous phase with hexane for 2,4-D or 2,4,5-T or ether for picloram and chromatographed on Florosil (5% H_2O wt/wt) generally as described by Bevenue *et al.* (5). Samples were analyzed for herbicide content by gas chromatography (20).

Amitrole. Amitrole was extracted in a Soxhlet extractor with 70 percent methanol for 20 hours. The extract was placed on a 65 g Dowex-50, 50- to 100-mesh ion exchange resin washed in turn with 100 ml methanol, 150 ml acetone, 150 ml hexane, 150 ml acetone, and 500 ml water.

The remainder of this method is essentially the same as outlined by Sutherland (25) except for his acetonitrile step. The data were corrected for recovery from zero-time samples and the results expressed as percent recovery as a function of time after treatment. These tests were designed as a series of factorial experiments with three replications. The factors were "time after treatment" and "chemicals applied." A separate factorial analysis of variance was used for recovery data for each herbicide.

When analysis of variance revealed significant differences (5% level) among recoveries for the factor "chemicals applied," specific tests of hypotheses were made. Differences among mean percent recovery values at the last sampling time usually were tested for significance (5% level) by the method of individual degrees of freedom (15).

Results and Discussion—Current Research

The degradation of 2,4-D, 2,4,5-T, and other herbicides in alder forest floor material has recently been investigated. In these studies, the incubation environment included a longer day length and a higher temperature (see "Materials and Methods") than used in previous studies. Sampling was also extended to magnify differences in degradation rate.

The first test of this series determined the degradation of amitrole, 2,4-D, and 2,4,5-T applied at 2.24 kg/ha (2 lb/acre) and picloram at 0.56 kg/ha (0.5 lb/acre) (Figure 6). Picloram, 2,4-D, and 2,4,5-T were applied in water as the potassium salt and amitrole in water as the parent herbicide.

Amitrole and 2,4-D were rapidly degraded. At 35 days, 2,4-D recovery had fallen to 6 percent and that of amitrole to 20 percent. In contrast, 2,4,5-T required 120 days to reach a recovery level of 13 percent. Picloram was even more resistant to degradation, and after 180

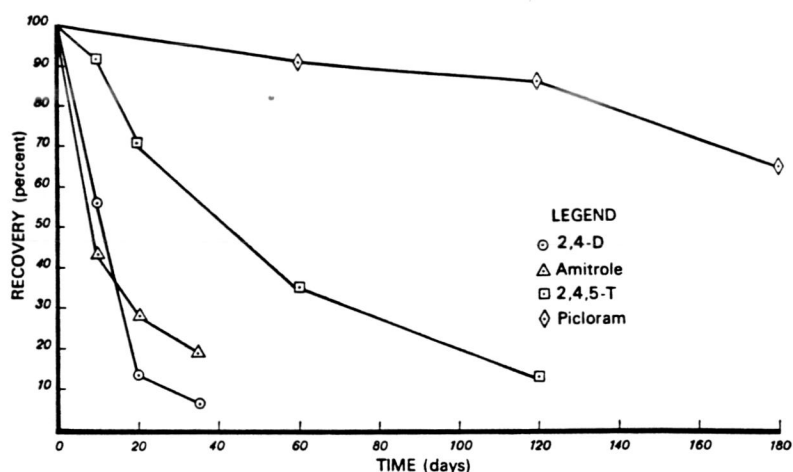


Figure 6. Recovery of 2,4-D, 2,4,5-T, amitrole, and picloram from red alder forest floor material.

days 65 percent remained in the litter. The degradation characteristics of each of these herbicides will be considered in more detail.

Degradation of 2,4-D

The influence of rate of application, presence of other herbicides, and pretreatment with insecticides on the persistence of 2,4-D was determined in the treatments indicated in Table 1. With only one exception, no significant differences were found in 2,4-D recovery at 35 days.

The percent recovery of 2,4-D applied at two rates is the same. That is, the half life (time to 50 percent decomposition) is independent of starting concentration, suggesting that the rate of degradation follows the first-order rate law. However, the rate constant was found to vary with time, which indicates deviation from first-order kinetics in this test period. This result is not surprising considering the multiple and sequential reactions possible in a heterogenous system.

Picloram and 2,4,5-T may cause initial slowing of the 2,4-D degradation rate; but by the 35th day, total degradation is the same as for 2,4-D alone. The persistence characteristics of 2,4-D in the field probably will not be greatly altered by either 2,4,5-T or picloram.

In another test, samples were pretreated with representatives of classes of insecticides—DDT (a chlorinated hydrocarbon), carbaryl (a carbamate), and phosphamidon (an organic phosphate). No significant differences were found among 2,4-D recoveries at 35 days

except between 2,4-D alone and 2,4-D plus carbaryl. This small reduction in 2,4-D degradation is not important in field use.

Norris and Greiner (20) (Figure 5) previously showed that the rate of degradation of 2,4-D increased when 2,4-D was applied with DDT. However, in the current test no such effect was evident, suggesting that enhancement is of short duration and occurs when the herbicide is applied with the insecticide.

The potential for alteration of 2,4-D persistence when applied to areas previously treated with these three insecticides is small. This relationship will also probably be true for many other insecticides of the chlorinated hydrocarbon, carbamate, and organic phosphate classes.

Table 1. RECOVERY OF 2,4-D FROM RED ALDER FOREST FLOOR MATERIAL

Treatment	Recovery of 2,4-D* (days after treatment)		
	10	20	35
	%	%	%
2,4-D—2.24 kg/ha (control)	56	14	6
2,4-D—4.48 kg/ha	65	16	5
2,4-D—2.24 kg/ha with 2,4,5-T—2.24 kg/ha	58	21	8
2,4-D—2.24 kg/ha with picloram—0.56 kg/ha	62	14	5
2,4-D—2.24 kg/ha one month after DDT—1.12 kg/ha	45	19	9
2,4-D—2.24 kg/ha one month after phosphamidon—1.68 kg/ha	55	20	6
2,4-D—2.24 kg/ha one month after carbaryl—2.24 kg/ha	51	15	11

* Recoveries at 35 days were not significantly different (5% level) except between 2,4-D applied alone (control) and 2,4-D applied after carbaryl.

Degradation of 2,4,5-T

The degradation of 2,4,5-T was determined at two rates of application and in the presence of another herbicide (Table 2). Mean recoveries did not differ significantly at 120 days. Degradation of 2,4,5-T appears to follow first-order kinetics when recoveries at two concentrations are compared. Like 2,4-D, however, the rate constant varies with time, showing deviation from the first-order rate law. A lag period, characteristic of the degradation of other herbicides, is found also with 2,4,5-T. The rate of breakdown of 2,4,5-T may be accelerated by 2,4-D up to 60 days; but after 4 months, recovery is the same as from the control.

Table 2. RECOVERY OF 2,4,5-T FROM RED ALDER FOREST FLOOR MATERIAL

Treatment	Recovery of 2,4,5-T* (days after treatment)		
	20	60	120
	%	%	%
2,4,5-T—2.24 kg/ha (control)	66	35	13
2,4,5-T—4.48 kg/ha	78	42	18
2,4,5-T—2.24 kg/ha with 2,4-D—2.24 kg/ha	78	24	13

* Recoveries at 120 days were not significantly different at the 5 percent level.

Degradation of amitrole

Amitrole was applied at two rates and with other chemicals (Table 3). Mean recoveries were not significantly different among the various treatments, indicating that neither 2,4-D nor ammonium thiocyanate are likely to influence the persistence of amitrole in the field.

Degradation of picloram

Picloram is a relatively new herbicide of considerable potential use in forestry. It is normally applied at a lower rate than 2,4-D or 2,4,5-T but frequently in combination with them.

Picloram was applied at 0.56 kg/ha with and without 2,4-D at 2.24 kg/ha. There was no significant difference between mean recoveries for the two treatments (Table 4). A lag period in the degradation

Table 3. RECOVERY OF AMITROLE FROM RED ALDER FOREST FLOOR MATERIAL

Treatment	Recovery of amitrole* (days after treatment)			
	5	10	20	35
	%	%	%	%
Amitrole—2.24 kg/ha	47	42	28	20
Amitrole—4.48 kg/ha	54	39	29	21
Amitrole—2.24 kg/ha with NH ₄ SCN—2.02 kg/ha†	51	48	31	20
Amitrole—2.24 kg/ha three weeks after 2,4-D— 2.24 kg/ha	57	50	25	24
Amitrole—2.24 kg/ha with 2,4-D—2.24 kg/ha	57	43	26	21

* Recoveries among treatments were not significantly different at the 5 percent level.

† This combination of chemicals is amitrole-T.

of picloram is suggested by an increase in the rate of degradation between 120 and 180 days in both treatments. Hamaker *et al.* (11) report that picloram degradation follows half-order kinetics.

Table 4. RECOVERY OF PICLORAM FROM RED ALDER FOREST FLOOR MATERIAL

Treatment	Percent recovery of picloram* (days after treatment)		
	60	120	180
	%	%	%
Picloram—0.56 kg/ha	92	87	65
Picloram—0.56 kg/ha with 2,4-D—2.24 kg/ha	82	77	59

* Recoveries between treatments were not significantly different at the 5 percent level.

Mechanisms of degradation

The recovery of 2,4-D, 2,4,5-T, and amitrole was studied in forest floor material which was steam-sterilized at 1.05 kg/cm² for 30 minutes (15 lb/in²) and maintained under aseptic conditions. Little degradation of 2,4-D or 2,4,5-T occurred during the 20-day test period, showing the microbial nature of the degradation process. The recovery of amitrole was only slightly different in sterile and normal material (Figure 7). In an earlier test (21), the recovery of amitrole was the same from sterile and normal material.

In another study, steam-sterilized and normal forest floor material in cotton-plugged flasks was treated with amitrole-5-¹⁴C (2.3 mg amitrole, 0.25 μ C ¹⁴C per flask), and the recovery of radioactivity and amitrole was determined. After five days of incubation under aseptic conditions, total CO₂ evolution was reduced 92 percent in the steam-sterilized litter. Chemical analysis showed 34 percent recovery of amitrole from normal and 45 percent from sterile forest floor material. Nearly 28 percent of the applied radioactivity was recovered as ¹⁴CO₂ from normal material, but less than 0.1 percent from sterile material. These data show that, despite nearly complete absence of biological activity, the degradation of amitrole proceeds at a near normal rate.

The radioactivity left in both the normal and sterile samples after methanol extraction was not released in appreciable quantities by acid digestion at room temperature for 16 hours. Ashton (1) also reported the formation of an alcohol-insoluble product from amitrole in sterile soil. Plimmer *et al.* (22) reported the chemical degradation of amitrole by a free radical-generating system. Contrary to the find-

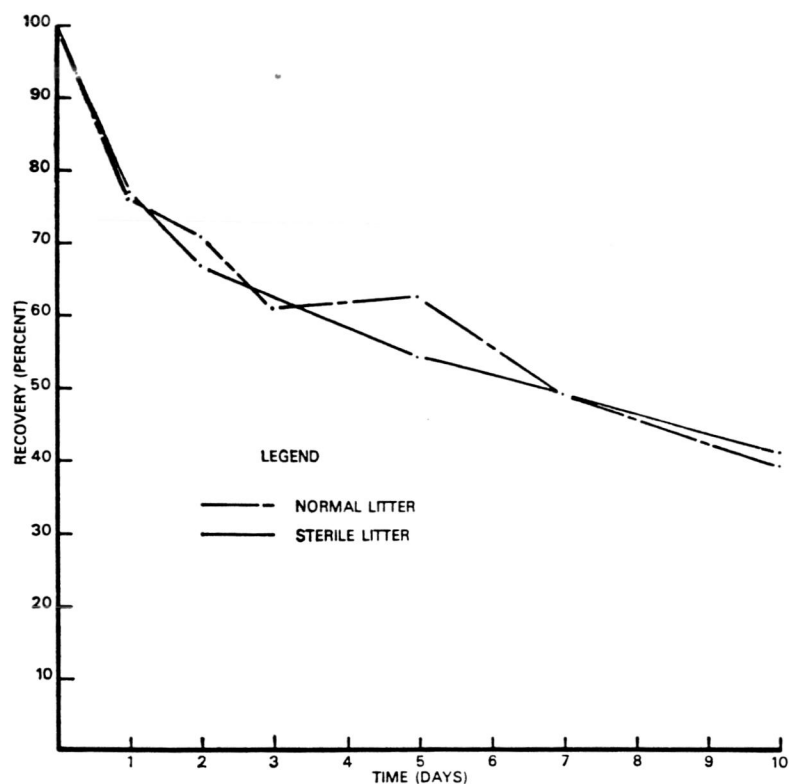


Figure 7. Recovery of amitrole in sterile and fresh red alder forest floor material.

ings of Riepma (23), these data indicate that an appreciable part of the degradation of amitrole can be nonbiological in nature.

Summary and Conclusions

The research reported here establishes that 2,4-D, 2,4,5-T, amitrole, and picloram are degraded in forest litter but at markedly different rates. The degradation of 2,4-D differs slightly in litter from different vegetation types, but these differences will not be significant in the field. Constituents of formulation may retard the degradation rate of 2,4-D. Picloram, 2,4,5-T, and diesel oil do not influence the rate of degradation of 2,4-D. Similarly, application of DDT, phos-

phamidon, or carbaryl one month prior to application of herbicide has no effect on 2,4-D degradation. When 2,4-D and DDT are applied together, the degradation rate of 2,4-D is stimulated.

Although 2,4,5-T is somewhat more persistent than 2,4-D, it approaches 90 percent degradation after four months. The degradation of 2,4,5-T is not influenced greatly by concurrent application of 2,4-D.

Amitrole has an initial rate of degradation exceeding that of 2,4-D and is rapidly lost in the forest floor. Amitrole degradation is not completely biological, as shown by abundant loss in steam-sterilized material. Neither ammonium thiocyanate, applied with amitrole in the proportions found in the herbicide amitrole-T, nor 2,4-D have any effect on the degradation of amitrole.

Picloram is considerably more resistant to degradation than the other herbicides studied, but it is biodegradable. Picloram and 2,4-D applied together at rates proportional to those found in a commercial formulation have no effect on picloram degradation.

The recovery of 2,4-D, 2,4,5-T, and amitrole appears to follow first-order kinetics with respect to concentration, but the order of kinetics clearly changes with time. Mixed-order kinetics may reflect changes in availability of herbicide or efficiency of its utilization by microorganisms.

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