The Degradation of 2, 4-D in Forest Litter[1]

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Introduction

According to a recent survey (1), more than 100 million acres of commercial forest land in the United States are either "nonstocked" or "poorly stocked" with trees of acceptable quality or species. Herbicides have become increasingly important tools for keeping forest lands in full production. However, the safe use of these chemicals requires a knowledge of their behavior in the environment.

The forest litter is a major receptor of residues of aerially applied herbicides due to spray penetration of the overstory vegetation, rain-washing of treated surfaces and abscission of treated foliage. The extent of stream contamination

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by chemicals depends in some degree on the persistence and movement of herbicides in the environment of the forest floor. The behavior of some herbicides has been extensively studied in agricultural soils (2), but little work has involved the forest environment. Evans and Smith (3) isolated an organism from coniferous litter which was able to use some phenoxy herbicides as substrates. Norris (4) showed that 2,4-D and 2,4,5-T are degraded in forest litter but at different rates. The purpose of the present study was to determine the influence of forest litter type and several chemical factors on the persistence of 2,4-D in forest litter.

Methods and Materials

Forest litter from Douglas-fir, *Pseudotsuga menziesii* (Mirb.) Franco.; bigleaf maple, *Acer macrophyllum* Pursh.; vine maple, *Acer circinatum* Pursh.; ceanothus, *Ceanothus velutinus* var. *laevigatus* How.; and red alder, *Alnus rubra* Bong. vegetation types was collected in western Oregon in June, 1965. The litter was mechanically chopped then preconditioned for three weeks in a growth chamber environment of a 12 hour day with 42° F night and 62° F day temperature to simulate conditions in coastal Oregon during the early spring. Twenty gram (oven dry weight) samples were then weighed into four-ounce waxed paper cups which were returned to the growth chamber immediately after the appropriate treatments had been applied. The environmental conditions during the test period were the same as those used during the preconditioning period.

A completely randomized 5 x 10 factorial design with two replications was used in this study. The treatments and time after treatment were designated as the two sets of factors.

In one treatment series, litter of each type collected was treated with the equivalent of 3 lbs./A. a.e. of the triethanol amine salt of 2,4-D. In a second series, alder litter only was treated with 3 lbs./A. a.e. of pure 2,4-D acid (in water with sufficient ethanol to effect solution), the isooctyl ester of 2,4-D (commercial formulation) or a solubilized acid formulation of 2,4-D (commercial formulation). In a third series, alder litter only was treated with 3 lbs./A. a.e. of the isooctyl ester of 2,4-D plus the equivalent of 1 lb./A. of DDT or 4 gal./A. of diesel oil. All treatments were applied in water.

At 0, 3, 6, 10 and 15 days after treatment, samples were removed from the growth chamber and frozen until analyzed. The samples were homogenized in 1 N NaOH and digested for 4 hours on a steam bath. The mixture was centrifuged while hot, the liquid decanted, and the residue resuspended and contrifuged twice with 100 ml aliquots of hot 1 N NaOH. The supernatants were combined, acidified to pH 1 and extracted overnight with benzene in a liquid-liquid extractor. The benzene extract was evaporated to dryness and esterified by heating for five minutes with 10% BF_3-methanol solution. After water was added, the ester was extracted into benzene.

Aliquots of the benzene extract were injected into a gas chromatograph for quantitative determination of the herbicide. A 6' x 1/4" glass column packed with 5% ethyl acetate fractioned Dow HiVac Silicon on 70/80 mesh Gas Chrom Z or a 4' x 1/4" glass column packed with 5% Dow 11 on 70/80 mesh Gas Chrom Z, operated at 175 and 165^{o} C respectively, were used in a Dohrmann gas chromatograph. This procedure gave 2,4-D recoveries of 77% from spiked check samples.

The results are expressed as percent recovery as a function of time after treatment. The recovery at any time is relative to the amount of 2,4-D recovered from samples harvested immediately after treatment. The data, including values for all treatments and harvest dates, were subjected to analysis of variance followed by analysis for differences among recoveries 15 days after treatment by the method of individual degrees of freedom according to Li (5).

Results and Discussion

Effect of Litter Type on Degradation of 2,4-D. Results from the first treatment series, in which various litter types were treated with 2,4-D triethanol amine, indicate apparent differences among types of litter in the degradation rate of 2,4-D (Fig. 1).

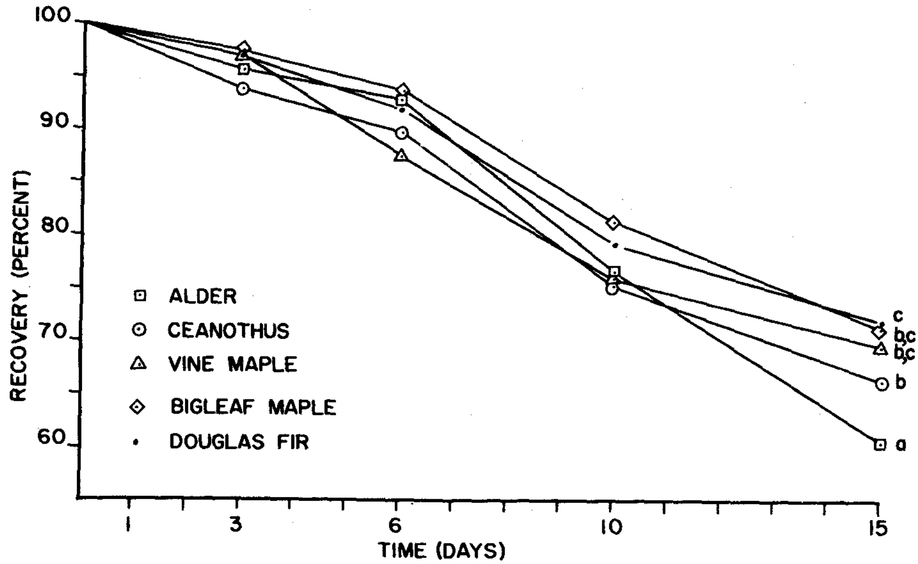

Figure 1. Recovery of 2,4-D from various types of forest floor litter following treatment with 3 lb/A. a.e. 2,4-D triethanol amine salt.

Recoveries at 15 days which have a letter in common are not significantly different at the 5% level.

However, with the possible exception of the alder litter type, these differences do not appear to be important from a practical standpoint. Variation in the degradation rate of 2,4-D in various litter types in the field may occur, but such variation is more likely to be a function of the microenvironment of the site than of the litter type.

Effect of Formulation on Degradation of 2,4-D in Alder Litter. In the second treatment series, which was concerned with the influence of formulation on 2,4-D degradation, alder litter was treated with 3 lbs./A. a.e. of pure 2,4-D acid, solubilized 2,4-D acid, the isooctyl ester or triethanol amine salt of 2,4-D. The data (Fig. 2) indicate that some significant differences exist among degradation rates of these four formulations.

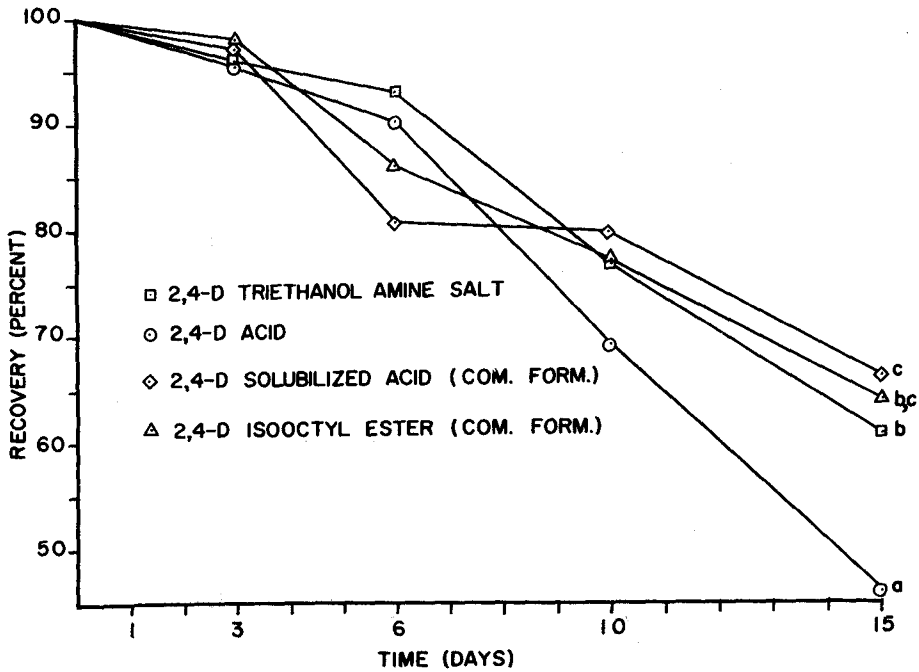

Figure 2. Recovery of 2,4-D from alder litter following treatment with 3 lb/A. a.e. 2,4-D acid, 2,4-D triethanol amine salt, 2,4-D isooctyl ester or 2,4-D solubilized acid formulations.

Recoveries at 15 days which have a letter in common are not significantly different at the 5% level.

It is interesting to note that the pure acid applied in water and a little alcohol was most readily degraded; the commercial formulation of solubilized acid was least readily degraded, and the degradation rate of the triethanol amine salt was intermediate.

The two acid and one amine salt 2,4-D formulations exist in the litter or soil solution in exactly the same chemical form, the degree of ionization depending on the pH of the solution. This fact gives some insight into the mechanism which causes the rate of 2,4-D decomposition to vary with the formulation. We believe that the differences in rates of decomposition of 2,4-D noted among the pure acid, the solubilized acid and the triethanol amine salt are due primarily to constituents of formulation such as emulsifiers, solvents and excess triethanol amine. Fletcher (6) has indicated for instance that triethanol amine is not a biologically inert solvent and, indeed, has been shown to inhibit the development of some fungi.

Because we are dealing with covalent rather than ionic bonds, the ester must be considered separately. It has been demonstrated that ester and amine formulations of 2,4-D behave differently in soil (7). The partition between organic and aqueous materials will vary with these formulations, and thus until the ester is hydrolyzed some differences in 2,4-D degradation would be expected. The effect of constituents of formulation are also likely to be involved in determining the rate of disappearance of the ester.

Effect of DDT and Diesel Oil on Degradation of 2,4-D in Alder Litter. The third treatment series concerned the influence of DDT and diesel oil on 2,4-D persistence in alder litter. This interaction is of interest because 2,4-D might be applied on areas previously treated with DDT, and because diesel oil is commonly used as a carrier for certain phenoxy herbicide formulations.

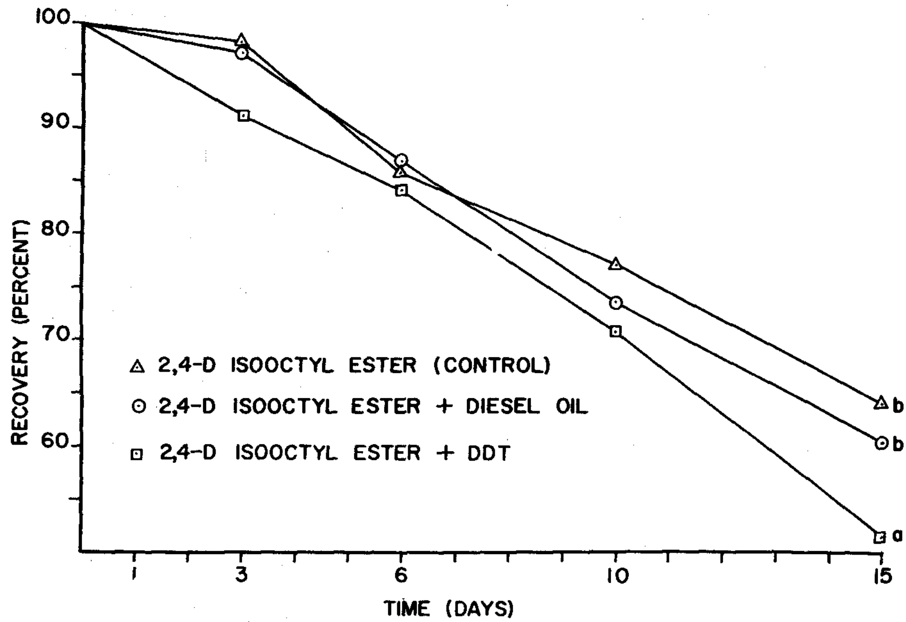

Figure 3. Recovery of 2,4-D from alder litter following treatment with 3 lb/A. a.e. of 2,4-D isooctyl ester alone or in combination with 1 lb/A. of DDT or 4 gal/A. of diesel oil.

Recoveries at 15 days which have a letter in common are not significantly different at the 5% level.

The results from this part of the study (Fig..3) indicate that diesel oil may have a slight stimulatory effect on 2,4-D degradation although the interaction was not statistically significant in this test. The fact that diesel oil does not appear to retard the degradation of 2,4-D is important since considerably more diesel oil than herbicide is applied per acre in some types of treatments.

The presence of DDT stimulated 2,4-D degradation. Some studies have indicated that DDT may increase the number of organisms in soil (8,9). In this case it is possible that the presence of DDT resulted in a more rapid adaption to the use of 2,4-D as a substrate by the microbial population, caused a more rapid build up of their number or both.

Summary

These studies have shown that 2,4-D is rapidly degraded in forest litter and that the rate of degradation varies with the type of litter, herbicide formulation and the presence of DDT. The degradation of 2,4-D varies slightly in litter from different vegetation types when incubated under similar environmental conditions. Greater variation in herbicide degradation rates may be expected in the field; but this will be due primarily to differences in the site microenvironment, rather than inherent differences in the litter.

Various formulations of 2,4-D are degraded at different rates in forest litter although we believe this to be more a function of constituents of formulation than a direct effect of the technical acid, salt or ester.

Finally, these experiments have shown that up to 4 gallons per acre of diesel oil has little or no effect on the decomposition of 2,4-D isooctyl ester, while 1 lb./A. of DDT appears to stimulate herbicide degradation.

Acknowledgment

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