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The movement, persistence, and fate of the phenoxy herbicides and TCDD in the forest

By

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I. Introduction

The phenoxy herbicides 2,4-dichlorophenoxyacetic acid (2,4-D), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), 2-(2,4-dichlorophenoxy) propionic acid (dichlorprop), 2-(2,4,5-trichlorophenoxy)propionic acid (silvex), and 2-methyl-4-chlorophenoxyacetic acid (MCPA) are important tools for weed and brush control.[1] They have played important roles in the culture of agricultural crops, forest and rangeland management, and a wide variety of noncropland weed control programs.

There has been increasing controversy about their safety since the late 1960s when 2,4-D and 2,4,5-T were used in Vietnam. More recently, questions have also been raised about their utility in achieving vegetation management objectives. In about 1969, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), a highly toxic trace contaminant, was reported in trichlorophenol-based pesticides such as 2,4,5-T and silvex. Most recently, the U.S. Environmental Protection Agency (EPA) has initiated administrative hearings regarding the future registration of 2,4,5-T and silvex. 2,4-D is also being evaluated by EPA in a process which could lead to similar hearings on that compound. Presumably all the phenoxy herbicides may ultimately be involved. The heart of this regulatory process is the risk-benefit assessment. While there is some argument about benefits from using phenoxy herbicides (including the utility of alternative chemical, fire, mechanical, and hand-labor methods for controlling unwanted vegetation), the central issue in the controversy is safety (risk assessment). This issue has been raised and argued most intensely in connection with the use of these herbicides in forestry.

An adequate evaluation of risk requires information about (1) the toxicology of the chemical, particularly dose-response relationships for acute and chronic responses, and (2) the magnitude and duration of exposure organisms will receive. These characteristics of exposure result from the behavior (*i.e.*, movement, persistence, and fate) of the chemical in the environment (NORRIS 1971).

This review compiles the published data on the behavior of phenoxy herbicides and TCDD in the forest environment. Emphasis has been given to studies done in the forest or which utilize substrates from the forest. References to studies in the agricultural environment or the

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[1] Mention of pesticides and proprietary products does not constitute an endorsement or recommendation for use by USDA nor does it imply registration under FIFRA as amended.

laboratory have been included as necessary to illustrate important concepts, to reinforce forest-oriented studies, or to bridge critical gaps in knowledge.

The *National Research Council of Canada* (1978) compiled an extensive monograph on the phenoxy herbicides. It is an excellent source of data, but it emphasizes the agricultural environment. A Society of American Foresters workshop on 2,4,5-T in forestry in 1977 produced six summary papers which covered the 2,4,5-T controversy, environmental behavior, toxicology, economics, and methods for managing vegetation in forest and rangelands (NORRIS 1977 a and b, SCHWETZ 1977, HONING and ROSS 1977, WALSTAD 1977, NEWTON 1977, DALEN 1977). These papers, along with those by DOST (1978), TURNER (1977), and YOUNG *et al.* (1978) and the symposium proceedings on chlorinated phenoxy acids from the Royal Swedish National Academy of Science (*Swedish National Scientific Research Council* 1978), provide good recent summaries on the phenoxy herbicides, but their emphasis is on 2,4,5-T and their scope extends beyond the forest environment. KIMMINS (1975) reviewed the ecological effects of herbicide usage in forestry, including some data on the behavior of phenoxy herbicides in the forest. Extensive bibliographies of the phenoxy herbicides and the substituted dibenzo-*p*-dioxins are also available (DIAZ-COLON and BOVEY 1976, 1977, and 1978, BOVEY and DIAZ-COLON 1977, 1978 a and b).

II. Characteristics of the forest and the use of phenoxy herbicides

The forest environment is quite different from the agricultural environment; therefore, the behavior and impact of the phenoxy herbicides in the forest are also likely to be different. Forest land is typically at higher elevations, receives more precipitation, and has steeper sloping land which is usually more fully occupied by vegetation on a year-round basis than is agricultural land. Forest soils are typically shallow, have a very high infiltration capacity, low pH, and high organic matter content, and are overlain by forest floor material consisting of a litter (L) layer on top of a partially decomposed (F) layer which is on top of a humus (H) layer.

The phenoxy herbicides are used extensively in forestry for a variety of vegetation control purposes. 2,4-D is the most commonly used herbicide in forestry. 2,4,5-T received its most extensive use there. Silvex, dichlorprop, MCPA, and the other phenoxy compounds receive much less use in the forest. It is difficult to determine accurately the annual use of phenoxy herbicides in forestry in the United States. The USDA Forest Service compiles data on the use of herbicides on National Forest land, and these data can be used as a guide to the relative amount of use among the various phenoxy herbicides.

Data for two time periods are included in Table I because the amount

Table I. *Use of phenoxy herbicides on National Forests.*[a]

Herbicide	Fiscal year 1976[b] Acres	Fiscal year 1976[b] Pounds	Fiscal year 1978[c] Acres	Fiscal year 1978[c] Pounds
2,4-D	136,195	240,204	183,465	246,530
2,4,5-T	53,251	102,720	4,161	6,841
dichlorprop	6,073	8,068	13,921	16,127
silvex	1,198	3,755	238	365

[a] Land administered by the USDA Forest Service as part of the National Forest System. 1 lb = 0.454 kg, 1 A = 0.405 ha.

[b] Derived from Pesticide Use Advisory Memorandum 167, April 14, 1967. USDA Forest Service, Washington, D.C. Covers 15 months, July 1, 1975 through September 30, 1976.

[c] Derived from Pesticide Use Advisory Memorandum 219, May 18, 1979. USDA Forest Service, Washington, D.C. Covers 12 months, October 1, 1977 through September 30, 1978.

of use has changed as public pressure and administrative, regulatory, and judicial processes have influenced decision-makers. The use of 2,4,5-T in particular has been affected. Table II shows the level of use of this herbicide from fiscal years 1971 through 1978.

Phenoxy herbicides are applied to the forest in a variety of forms by several types of equipment. The following is a list of typical phenoxy herbicide application techniques in forestry in a decreasing order of occurrence and importance:

Table II. *Use of 2,4,5-T on National Forests*[a]*, fiscal years 1971–1978*[b].

Fiscal year	Pounds	Acres
1971	57,402	25,777
1972	40,501	32,100
1973	53,220	26,424
1974	26,022	37,436
1975	95,540	49,357
1976	102,720	53,251
1977	14,597	7,105
1978	6,841	4,167

[a] Land administered by the USDA Forest Service as part of the National Forest System. 1 lb = 0.454 kg, 1 A = 0.405 ha.

[b] Derived from USDA Forest Service Pesticide Use Advisory Memorandum 210, October 26, 1978.

1. Aerial application of liquids by helicopter.
2. Ground application of liquids by high-volume, low-pressure sprayers or low-volume, high-velocity mist blowers.
3. Injection or basal application of liquids into or on individual tree stems.

Applications may be made at almost any time of the year, but dormant season applications just before or at bud break and foliage applications as full foliage expansion occurs or at the end of the growing season are most common. The formulations used and the methods, time, and rate of application all depend on the management objective and the density and species composition of the vegetation (Newton and Norris 1980).

III. The behavior of phenoxy herbicides in the forest

Phenoxy herbicides applied in the forest are distributed initially in the air, vegetation, forest floor, and surface waters. The exact proportion of spray material entering any of these four environments will vary with chemical factors (herbicide formulation and carrier), application factors (rates and volumes of application and the type of application equipment and its operating characteristics), climatological factors (wind speed and direction, relative humidity, and temperature), and several site factors (slope, aspect, elevation, vegetation type and density, and proximity to surface water). This concept of the initial distribution of herbicide in the forest is intuitive because there is only a limited data base. Some studies report the concentration of herbicide in various forest compartments immediately after or at intervals after application, but mass-balance studies are lacking. The following sections consider the movement, persistence, and fate of the phenoxy herbicides in each of the main compartments of the forest.

a) Behavior in air

Phenoxy herbicides may be in the air as vapors or in fine droplets which do not settle in the target area. They may settle or be washed down by rain into adjacent areas, adsorb on a number of surfaces, or be decomposed by photochemical reactions. Little work in this area has been done in the forest.

The appearance of "box elder blight" in the early 1950s was one of the first symptoms in the forest of a problem which also plagued agriculture, *i.e.*, the offsite movement of growth-regulator chemicals (like the phenoxy herbicides). Phipps (1963 and 1964) conducted studies which showed 2,4-D was the probable causative agent, although his test could not rule out the possibility that other phenoxy herbicides (or growth-regulating chemicals) might also be involved. He noted abnormal growth characteristics on elms (*Ulmus* sp.) and ash (*Fraxinus* sp.) could be caused by 2,4-D. The 2,4-D source causing box elder blight is not known for certain, but agricultural use was implicated. The *National Research Council of Canada* (1978) monograph on phenoxy herbicides gives an extensive review of the data on herbicides in air from agricultural uses. The fate of pesticides in the atmosphere has been reviewed by several authors with considerable attention to concepts and some data, but the emphasis has been on insecticides, and the phenoxy herbicides have received little attention (WHEATLEY 1973, SEIBER *et al.* 1975, MOILANEN *et al.* 1975, SPENCER and CLIATH 1975, CREWS *et al.* 1975).

In the forest, NORRIS (1967), citing unpublished data of Norris, Newton, and Zavitkovski, reported on the application of low-volatile esters of 2,4,5-T in diesel oil by fixed-wing aircraft in a western Oregon forest. They found this application resulted in the deposit of 25 to 40% of the chemical at ground level in small openings in the forest canopy. The implication is that 60 to 75% of the herbicide was lost from the application zone. MAKSYMIUK (1963), however, reported more than 40% of aerially applied insecticide did not reach ground level when spray cards were within one tree-height of the nearest vegetation.

Fixed-wing applications of herbicide are not typical in forests. More commonly, applications are made by helicopters which fly relatively slowly and low with a resulting increase in herbicide deposit in the intended area. NORRIS *et al.* (1976 c and 1981), using filter paper interception discs, recivered 85 and 70% of helicopter-applied 4-amino-3,5,6-trichloropicolinic acid (picloram) and 2,4-D from spray interception discs located above the brush. Spray interception discs yielded recoveries of 71% for 2,4-D and 90% for picloram applied by helicopter in four powerline rights-of-way in forested areas of Oregon and Washington (NORRIS *et al.* 1976 a).

Only limited data are available on drift or deposition after application by mist blower. In a test done under nearly ideal conditions, NORRIS *et al.* (1976 d) reported 92% of the picloram and 97% of the 2,4-D applied by a large truck-mounted mist blower was deposited in a 32.9-by-67-m test grid. BRADY and WALSTAD (1973) found 2,4,5-T at distances up to 150 m downwind from a sled-mounted mist blower based on herbicide deposit on spray cards or the response of herbicide-sensitive plants. Soybeans more than about 70 m from the line of application were not killed. HOLT *et al.* (1976) also studied mist-blower applications. They reported effects on plants at 440 m, but the spray mixture used contained both picloram and 2,4,5-T. At 240 m, epinasty was noted on sensitive plants suspended at 3.3-m intervals up to 12 m above the ground. With ground equipment in Texas, SCIFRES *et al.* (1977) reported 92% of the intended spray deposit (2,4,5-T and picloram) was recovered on mylar cards at ground level.

Both fine spray particles (drift) and vapors of phenoxy herbicide esters may move from target areas during and shortly after application. There is little data from the forest environment. In an agricultural setting

Grover *et al.* (1972) applied butyl ester and dimethylamine salt formulations of 2,4-D by ground equipment that resulted in only 2.8% of the total spray having a particle size less than 200 μm and only 3 to 4% of the spray drifted. However, 25 to 30% of the butyl ester was collected as vapor 75 m downwind 30 min after application. The butyl ester is substantially more volatile than the esters [2-ethylhexyl, butoxyethanol, isooctyl, propylene glycol butyl ether (PGBE)] used in forestry, but these findings indicate more studies of phenoxy herbicide ester volatility in the field are needed.

Spray drift was monitored in connection with an operational aerial application of 2,4-D low-volatile ester on the Chippewa National Forest in Minnesota. The amount of 2,4-D deposited on exposed trays 15 m from the treatment unit boundary was 50 to 90% less than the deposit inside the unit. This suggests only limited offsite movement of herbicide occurred. Residues ranged from 0.0005 to 0.1 kg/ha at 15 m (*Minnesota Department of Natural Resources* 1977).

These reports do not indicate actual residue levels in air, but they indicate that residues are present (at least for short periods of time) at concentrations sufficient to cause effects on sensitive plant species. **Lavy** (1979) measured 2,4,5-T in air as part of a study to evaluate applicator exposure. Only those workers involved with application by backpack sprayer or tractor-mounted mist blower received exposure to measurable amounts of 2,4,5-T via the air. The concentration in air ranged from not detectable (<0.004 μg/L) to 0.169 μg/L; the mean value was 0.02 μg/L. **Cheney** *et al.* [not dated] used motorized samplers and a resin to monitor 2,4,5-T residues in the air at intervals after aerial application of 3.36 kg/ha 2,4,5-T as the PGBE ester. They found detectable residues in air within the sprayed area for three wk after application. In general the levels were higher in samples collected between 1200 and 1400 hr than between 0700 and 0900 hr. The residues were highest the first 24 hr after application and then were substantially lower. No residues were detected 32 days after application (Table III). Presumably, the residue levels in air decline rapidly after application ceases because (1) fine particles settle out, (2) vapor production slows or ceases as ester hydrolysis occurs, and (3) the air mass is exchanged with fresh air.

The paucity of data on phenoxy herbicide residues in air in connection with forest spray operations indicates this is a significant gap in knowledge. Improving theory and methodology and a more extensive literature on this topic for agricultural situations suggest future studies in the forest will be easier to conduct and interpret.

b) Behavior in vegetation

The behavior of phenoxy herbicides in vegetation is discussed in three sections. The first and second sections consider the initial distribution and concentration of chemical in the canopy as a means of establishing

Table III. *Levels of 2,4,5-T in air after application of 3.36 kg/ha 2,4,5-T as PGBE ester.*[a]

Time after application (days)	Time of day	2,4,5-T ester ($\mu g/m^3$)
0	1000–1200	faulty measure
	1200–1400	0.679
1	0700–0900	0.117
	1200–1330	0.895
3	0650–0850	0.033
	1200–1400	0.175
8	0700–0900	0.012
	1200–1400	0.029
15	0700–0900	0.017
	1200–1400	0.017
21	0700–0900	$<$0.008
	1200–1400	0.054
32	0700–0900	$<$0.008
	1200–1400	$<$0.008

[a] CHENEY *et al.* [not dated].

maximum initial residue levels which are likely to occur during or shortly after application. The third section covers the persistence characteristics of the phenoxy herbicides to establish the residue levels as they change over time. Nearly all the data in both sections are from actual or simulated aerial application of herbicide. Little work has been done to characterize the distribution patterns which result from broadcast or selective ground application systems or procedures.

1. Initial distribution in the canopy.—The amount of the herbicide intercepted by vegetation varies with the rate and nature of the application and the type and density of the vegetation. ALTOM and STRITZKE (1972) found 33% of aerially applied 2,4-D, dichlorprop, and 2,4,5-T penetrated the overstory, and 13% reached the forest floor in a blackjack (*Quercus marilandica*) and a post oak (*Quercus stellata*) forest. The implication is that 20% of the material was intercepted by understory vegetation. In a similar forest type BOUSE and LEHMAN (1967), using nontoxic spray materials, found overstory penetration of 19 to 22% while penetration through the understory was 4 to 6%, indicating about 15% interception. TSCHIRLEY (1968) found about 21% of aerially applied phenoxy herbicides penetrated the upper canopy and 6% penetrated to ground level in tropical and subtropical forests. The percent spray penetration was inversely related to canopy density.

2. Concentration in vegetation immediately after application.—NORRIS *et al.* (1977) looked at the initial distribution of 2,4,5-T low-volatile ester in oil applied by helicopter to a mixed hardwood brush community in northwest Oregon. They found marked contrast in the concentration of 2,4,5-T among various species shortly after application which indicates the nature of the intercepting surface is also important (Table IV). For instance, 11 mg/kg of 2,4,5-T was on vine maple (*Acer circinatum*) compared to 120 mg/kg on grass. The vine maple buds were swollen but foliage had not yet expanded, thus they had a relatively small surface-to-mass ratio at the time of application. Grass, on the other hand, had a large surface area relative to its mass, and the concentration of herbicide was high.

When blackberry foliage (*Rubus* sp.), grass, and vine maple were re-treated one yr later, the initial herbicide concentrations were higher (Table IV). This reflects a general decrease in the density of overstory vegetation from the yr before. The initial concentration on Douglas-fir (*Pseudotsuga menziesii*) was about the same in both yr, probably because the individual trees sampled were growing in the open and the overstory density did not change from one year to the next.

In a study in West Virginia, NORRIS *et al.* (1978) found initial residue levels of 2,4,5-T on four kinds of vegetation ranging from 300 mg/kg on blackberry foliage to 80 mg/kg on greenbriar (Table IV) after helicopter application of 2.24 kg/ha ae as butoxyethanol ester. WELLENSTEIN (1975 a and b) measured residues of 2,4,5-T on foliage of several species after helicopter application of ester formulation in Europe. Extrapolating from a graph, initial concentrations ranged from 40 mg/kg on hazel to 500 mg/kg on oak and spruce (Table IV). These values for oak and spruce presumably reflect their dominant position in the canopy, while the lower values for birch (60 mg/kg) and hazel more nearly reflect the levels reported by others for understory vegetation. The initial residue levels are difficult to interpret because the rate of application was not specified.

PLUMB *et al.* (1977) reported initial herbicide concentrations of 95 and 92 mg/kg of 2,4-D and 2,4,5-T, respectively, in chamise (*Adenostoma fasiculatum*) immediately after a simulated aerial application of 4.48 kg/ha ae of 2,4-D and 2,4,5-T in southern California (Table IV). RADOSEVICH and WINTERLIN (1977) reported about 19% of the spray material was on the overstory chamise plants immediately after ground-sprayer application of 4.5 kg/ha of 2,4-D or 2,4,5-T (as butoxypropyl ester). About 28% was on understory grass and forbs and 52% was on the litter (forest floor material). RADOSEVICH and WINTERLIN did not report actual residue values, but by calculation from their Table 2, initial residue levels were about 200 mg/kg on chamise and 300 mg/kg on grass and forbs immediately after application.

ERONEN *et al.* (1979) reported on the behavior of MCPA in a forest ecosystem. Residues of 344 mg/kg were found in birch twigs and leaves and 74 mg/kg in moss collected immediately after aerial application of 2.5 kg/ha of MCPA isooctyl ester (Table IV).

Grass is an important component of both forest and range ecosystems. Grass communities have potential for high herbicide concentrations because they are a relatively low-growing type of vegetation with a large surface-to-mass ratio. BOVEY and BAUR (1972) applied 2,4,5-T to a grass community at five locations in Texas and found initial herbicide residues ranged from 32 to 144 mg/kg for rates of application of 0.56 and 1.12 kg/ha ae (Table IV). MORTON *et al.* (1967) reported herbicide residue levels in grass ranged from 20 to 210 mg/kg (Table IV) immediately after simulated aerial applications of several formulations of 2,4,5-T and 2,4-D. Immediately after application of 2,4,5-T and picloram (1.12 kg/ha each) with ground equipment to range sites in Texas, SCIFRES *et al.* (1977) found 2,4,5-T residues in coastal bermuda grass ranged from 58 to 125 mg/kg (Table IV).

OLBERG (1973) and OLBERG *et al.* (1974), concerned about 2,4,5-T residues in wild raspberry fruits (species not identified), reported that initial herbicide concentrations ranged from 0.7 to 3.3 mg/kg 1 hr after treatment with 6 kg 2,4,5-T in 250 L water/ha in tests conducted in 1972. Apparently similar applications in 1973 produced initial 2,4,5-T residues ranging from 7.9 to 22.2 mg/kg. Applications in both cases were by "backpack power sprayer." In contrast, MAIER-BODE (1972) found only 1 mg/kg of 2,4,5-T on unidentified wild berries in Sweden on the day of treatment by aircraft. BROWN and MACKENZIE (1971) found residues of 2,4,5-T up to 100 mg/kg on unwashed blackberry fruits 3 days after spraying with 3 kg/ha of 2,4,5-T. Ripe fruits remained in good condition for about 3 days, but immature fruits failed to ripen.

These reports indicate initial phenoxy herbicide residues in forest vegetation can range up to about 300 mg/kg for rates of application up to 2.24 kg/ha ae. Proportionally higher residue levels may be expected for higher rates of application.

3. Persistence characteristics.—Phenoxy herbicide residues decline with time in forest vegetation through the action of several processes, including volatilization, photochemical or biological degradation on leaf surfaces, weathering (rain washing, cuticle erosion), absorption and translocation, growth dilution, metabolism, excretion, and others. Most field studies only determine residue levels and do not determine the importance of specific residue-reduction processes. The following paragraphs provide specific data on phenoxy herbicide residue levels in forest vegetation as a function of time after application. There are more data for 2,4,5-T than for 2,4-D. There are few reports on the persistence of other phenoxy herbicides in forest vegetation.

PLUMB *et al.* (1977) simulated the aerial application of 2,4-D and 2,4,5-T (PGBE ester, 4.48 kg ae each in 186 L of water/ha) to a 3-yr-old stand of chamise in southern California. 2,4-D and 2,4,5-T had half-lives of about 37 and 17 days in this vegetation (Table IV). The rate and extent of decline of these herbicide residues was not as great as is noted in some other studies, probably because the site was very dry. Plant moisture levels were about half of normal at the time of application and declined to less than 30% 9 wk after the application. This largely eliminated metabolism of the residues. About 3 mg/kg of 2,4-D and

2,4,5-T were present in the dead vegetation 1 yr after application. Sprouts from the treated plants did not show formative effects but did contain 0.27 mg/kg 2,4-D and 0.31 mg/kg 2,4,5-T 1 yr after application. These plant parts were not present at the time of application, indicating these residues resulted from the translocation of chemical from treated portions of the plant.

RADOSEVICH and WINTERLIN (1977) also measured 2,4-D and 2,4,5-T residues in chapparal vegetation. They expressed their data relative to the total amount of herbicide recovered in vegetation, litter, and soil immediately after application of 4.5 kg/ha of each herbicide. They found residues declined rapidly (more than 90%) in the first 30 days after application, but then the rate of loss declined. Calculations based on their Table 2 suggested residues on vegetation were 0.1 to 0.2 mg/kg 1 yr after application.

NORRIS *et al.* (1977) determined residues of 2,4,5-T in 4 species of forest vegetation after two successive annual applications (4.48 kg/ha of 2,4,5-T ae as isooctyl ester applied in diesel oil by helicopter in March). A sharp decrease in herbicide concentration occurred the first mon after application, but the rate of residue disappearance slowed after 3 mon (Table IV). The mean half-life of 2,4,5-T for all species was about 2 wk after both the first and the second application. One yr after application, residues ranged from 0.48 mg/kg in vine maple to 0.07 mg/kg in blackberry foliage. On 3 plots which were not sprayed the second time, 2,4,5-T herbicide residues were below detectable limits in all species except vine maple 2 yr after the first application. The rate of decline of 2,4,5-T residues in vegetation after the second application was similar to the first except that 1 yr after the second application, no residues were detected in any of the sprayed vegetation. Thus, in this case at least, 2 successive annual applications of 2,4,5-T had no appreciable effect on the persistence of the herbicide in 4 different kinds of vegetation.

In West Virginia, residues of 2,4,5-T on 4 species declined rapidly after application (2.24 kg/ha 2,4,5-T ae as butoxyethanol ester applied in August by helicopter). The mean concentration was 150 mg/kg immediately after application and 25 mg/kg at 1 mon, 5 mg/kg at 6 mon, 0.07 mg/kg at 1 yr, and <0.01 mg/kg at 2 yr (Table IV). The initial rate of decline was slower in West Virginia than in a comparable study in Oregon (NORRIS *et al.* 1978).

WELLENSTEIN (1975 a and b) reported relatively rapid decline (90+% in 10 wk) in concentration of herbicide in foliage of 4 species of woody plants in a European forest treated with 2,4,5-T ester by helicopter. The rate of loss was slower after 10 wk, and residues ranged from 0.25 to 0.4 mg/kg 1 yr after application (Table IV). ELIASSON (1973) applied butoxyethyl ester of 2,4-D to young aspen trees (*Populus* sp.) in a glasshouse experiment and found a marked decrease in herbicide residue level with time, despite the fact an extremely high concentration of herbicide was present initially, and more than half the sprayed leaf tissue was dead after 9 days (Table IV).

Table IV. *Phenoxy herbicide residues in vegetation.*

Herbicide	Location	Plant species	Application	Residue level in mg/kg (days after application)	References
2,4-D	So. Calif.	Chamise	3.4 kg/ha ae PGBE ester in water, simulated aerial application, May	95(0) 70(14) 69(29) 20(69) 16(146) 3.8(379)	PLUMB *et al.* (1977)
2,4-D	So. Calif.	Chamise	4.5 kg/ha ae butoxy propyl ester in water, ground sprayer, April and May	221(0) 60(30) 35(60) 22(90) 12(180) 0.1(360)	RADOSEVICH & WINTERLIN (1977)
2,4-D	So. Calif.	Grass and forbs	4.5 kg/ha ae butoxy propyl ester in water, ground sprayer, April and May	269(0) 21(30)	RADOSEVICH & WINTERLIN (1977)
2,4-D	Texas	Grass	1.12 kg/ha ae 2,4-D amine in water, simulated aerial application, June	80(0) 70(7) 45(14) 30(28) 6(56) 1(112)	MORTON *et al.* (1967)
2,4-D	Sweden	Poplar	Glass house application, 2,4-D butoxyethyl ester in diesel oil	2300(1) 2500(3) 1800(9) 1300(37) 870(365)	ELIASSON (1973)
2,4-D	Sweden	Cowberry and bilberry	0.25 kg/ha ester, ground application	0.3(34) and 0.1(29)	RAATIKAINEN *et al.* (1979)
			0.75 kg/ha	1.0(35) and 1.3(29)	
			2.25 kg/ha	3.7(35) and 4.8(29)	
2,4,5-T	Texas	Grass	1.12 kg/ha ae PGBE ester in water, simulated aerial application	73(0) 2.1(42) 0.02(182)	BOVEY & BAUR (1972)
2,4,5-T	Sweden	Cowberry and bilberry	0.25 kg/ha ester, ground application	0.5(34) and 0.4(29)	RAATIKAINEN *et al.* (1979)
			0.75 kg/ha	1.2(35) and 1.3(29)	
			2.25 kg/ha	3.9(35) and 2.5(29)	
2,4,5-T	Germany	Raspberry (fruits)	6 kg/ha formulation not known, in water, foliage application from ground, June & July	16(0) 11.2(5) 3.4(15) 1.5(30) (by interpolation, Table 2)	OLBERG *et al.* (1974)

2,4,5-T	Texas	Live oak (stem tips)	2.24 kg/ha ae 2,4,5-T isooctyl ester in water, simulated aerial application, June	9.6(30) 0.7(180)	Baur *et al.* (1969)
2,4,5-T	Texas	Grass	2.24 kg/ha ae 2,4,5-T isooctyl ester in water, simulated aerial application, June	7.0(30) 0.2(180)	Baur *et al.* (1969)
2,4,5-T	Texas	Coastal bermuda grass	1.12 kg/ha ae (formulation not specified) in 127 L/ha of diesel oil:water (1:4) with ground sprayer	246(0) 7.9(7) 4.9(28) 0.42(56) 0.05(112) 0.005(365) (average values from Table 1)	Scifres *et al.* (1977)
2,4,5-T	Europe	Raspberry fruits	6 kg/ha Tormona salt in water, backpack sprayer	8.3(0) 8.1(4) 7.8(7)	Eichler & Leber (1975)
2,4,5-T	Europe	Raspberry foliage	6 kg/ha Tormona salt in water, backpack sprayer	368(0) 19(7) 28(13) 15(21) 5(36) 4(51) 2(83)	Eichler & Leber (1975)
2,4,5-T	Europe	Grass	6 kg/ha Tormona salt in water, backpack sprayer	64(0) 8(7) 4(13) 3(21) 0.8(36)	Eichler & Leber (1975)
2,4,5-T	Europe	Blackberry fruits	2.5 L/ha Tormona 80 in water, helicopter	7.7(0) 8.3(4) 7.5(7)	Eichler & Leber (1975)
2,4,5-T	Texas	Grass	0.56 kg/ha ae 2,4,5-T butoxyethanol ester in water, simulated aerial application, June	48(0) 35(7) 10(14) 9(28) 7(56)	Morton *et al.* (1967)
2,4,5-T	Texas	Grass	2.24 kg/ha ae 2,4,5-T butoxyethanol ester in water, simulated aerial application, June	205(0) 150(7) 50(14) 60(28) 25(56)	Morton *et al.* (1967)
2,4,5-T	Oregon	Douglas-fir	2.24 kg/ha isooctyl ester in oil, helicopter application in early spring		Norris *et al.* (1977)
			First annual application	52(0) 11.1(30) 0.35(90) 0.47(180) 0.22(360) 0.0(720)	
			Second annual application	52(0) 14.2(30) 0.10(90) 0.04(180) 0.0(360)	

Table IV. (*Continued*)

Herbicide	Location	Plant species	Application	Residue level in mg/kg (days after application)	References
2,4,5-T	Oregon	Vine maple	First annual application	10.6(0) 0.48(30) 0.28(90) 0.16(180) 0.48(360) 0.02(720)	NORRIS *et al.* (1977)
			Second annual application	23.2(0) 10(30) 0.10(90) 0.10(180) 0.02(360)	
2,4,5-T	Oregon	Grass	First annual application	114(0) 3.4(30) 0.58(09) 0.14(180) 0.12(360) 0.0(720)	NORRIS *et al.* (1977)
			Second annual application	140(0) 9.3(30) 0.21(90) 0.12(180) 0.0(360)	
2,4,5-T	Oregon	Blackberry (vines & foliage)	First annual application	45(0) 0.59(30) 0.05(90) 0.02(180) 0.03(360) 0.0(720)	NORRIS *et al.* (1977)
			Second annual application	165(0) 2.9(30) 0.01(90) 0.0(180) 0.0(360)	
2,4,5-T	So. Calif.	Chamise	3.4 kg/ha ae, PGBE ester in water, simulated aerial application, May	92(0) 44(14) 32(29) 14(69) 2.9(146)	PLUMB *et al.* (1977)
2,4,5-T	So. Calif.	Chamise	4.5 kg/ha ae PGBE ester in water, ground sprayer, April and May	184(0) 13(30) 8(60) 10(90) 8(180) 0.2(360)	RADOSEVICH & WINTERLIN (1977)
2,4,5-T	So. Calif.	Grass and forbs	4.5 kg/ha ae PGBE ester in water, ground sprayer, April and May	319(0) 31(30)	RADOSEVICH & WINTERLIN (1977)
2,4,5-T	W. Virginia	Blackberry (foliage)	2.24 kg/ha ae butoxyethanol ester in water, helicopter application in August	289(0) 156(7) 48(30) 8.8(90) 3.4(182) 0.01(365) 0.003(730)	NORRIS *et al.* (1978)

2,4,5-T	W. Virginia	Greenbriar	2.24 kg/ha ae butoxyethanol ester in water, helicopter application in August	84(0) 28(7) 9.7(30) 4.3(90) 1.0(182) 0.03(365) 0.002(730)	Norris *et al.* (1978)
2,4,5-T	W. Virginia	Sassafras	2.24 kg/ha ae butoxyethanol ester in water, helicopter application in August	141(0) 33(7) 19(30) 8.1(90) 2.2(182) 0.016(365) 0.003(730)	Norris *et al.* (1978)
2,4,5-T	W. Virginia	Grass	2.24 kg/ha ae butoxyethanol ester in water, helicopter application in August	91(0) 28(7) 17(30) 11(90) 12(182) 0.22(365) 0.03(730)	Norris *et al.* (1978)
2,4,5-T	Europe	Spruce	Unspecified rate of ester by helicopter	500(0) 20(70) 1.5(210) 0.4(350) 0.1(665)	Wellenstein (1975 a and b)
2,4,5-T	Europe	Birch	Unspecified rate of ester by helicopter	60(0) 8(70) 1(210) 0.25(350) 0(665)	Wellenstein (1975 a and b)
2,4,5-T	Europe	Oak	Unspecified rate of ester by helicopter	500(0) 1.5(70) 0.4(210) 0.25(350) 0.1(665)	Wellenstein (1975 a and b)
2,4,5-T	Europe	Hazel	Unspecified rate of ester by helicopter	40(0) 5(70) 0.9(210) 0.32(350) 0.05(665)	Wellenstein (1975 a and b)
2,4,5-T	California	*Ceanothus* sp.	3.36 kg/ha as PGBE ester, helicopter application in October	147(0) 154(1) 95(3) 55(8) 10.5(15) 4.8(21) 8.5(32) 0.9(228) (combined ester and acid forms)	Cheney *et al.* [not dated]
MCPA	Sweden	Cowberry and bilberry	Ground application 0.25 kg/ha ester	0.2(34) 0.2(29)	Raatikainen *et al.* (1979)
			0.75 kg/ha ester	0.8(35) 0.7(29)	
			2.25 kg/ha ester	3.0(35) 3.9(29)	
MCPA	Finland	Birch leaves and twigs	Aerial application 2.5 kg/ha isooctyl ester	344(0) 119(15) 132(40) 25(261) 32(283) 44(297)	Eronen *et al.* (1979)
MCPA	Finland	Moss	Aerial application 2.5 kg/ha isooctyl ester	74(0) 17(15) 3(40) 0(283)	Eronen *et al.* (1979)

2,4,5-T was applied at 2.24 kg/ha as the 2-ethylhexyl ester alone or in combination with picloram to live oak (*Quercus virginia*) and native grasses by BAUR *et al.* (1969). They did not collect samples immediately after application but did show that 90 to 99% of the 2,4,5-T present in samples collected 1 mon after the treatment were no longer present in samples collected 6 mon after treatment. Persistence of 2,4,5-T was longer in plants treated with 2,4,5-T-picloram mixture than in plants treated with 2,4,5-T alone (Table IV). BOVEY and BAUR (1972) also looked for 2,4,5-T in range grass in Texas after application of herbicide at 0.56 and 1.12 kg/ha ae as PGBE ester in 186 L of water/ha in a simulated aerial application. A 98% reduction in 2,4,5-T levels was found 6 wk after application with nondetectable or nearly nondetectable levels reported 26 wk after application. Rainfall influenced the rate of loss of 2,4,5-T at different sites in this study. MORTON *et al.* (1967) found a sharp decrease in the levels of 2,4-D and 2,4,5-T in range grass treated with ester, acid, and amine formulations of these herbicides in simulated aerial applications at rates of 0.56, 1.12, or 2.24 kg/ha ae (Table IV). They reported no effect of formulation on persistence but that amount and frequency of rainfall were important. On coastal Bermuda grass treated with 1.12 kg/ha each of 2,4,5-T and picloram, 92% of the 2,4,5-T present immediately after spraying was gone in 7 days (Table IV) (SCIFRES *et al.* 1977). RADOSEVICH and WINTERLIN (1977), on the other hand, indicated rainfall 30 days after application was not a major factor in residue reduction on leaves. More than 90% of the herbicide had already disappeared from foliage in their study by 30 days. If the rain had reduced remaining residues by 50%, this loss may not have been easily detected.

Phenoxy herbicide esters are believed to hydrolyze rapidly on plant surfaces. SUNDSTROM *et al.* (1979) looked for both acid and ester forms of 2,4,5-T in foliage from brush vegetation treated by tractor sprayer (2 to 5 kg/ha ae 2-butoxyethyl ester) or airplane (1.5 to 3 kg/ha of isobutyl, butyl ester). Results were highly variable for samples from the tractor-sprayed areas reflecting the uneven initial distribution of herbicide. They found 640 mg/kg of 2-butoxyethel ester and 390 mg/kg of acid of 2,4,5-T 8 days after application. After 45 days, the levels were 180 mg/kg for both. Residues were generally lower in the aerially treated area. They averaged 38 mg/kg of butyl ester, 16 mg/kg of isobutyl ester, and 61 mg/kg of acid of 2,4,5-T 18 days after application. The rate of ester hydrolysis apparent in this study was not as rapid as has been reported by GLASTONBURY *et al.* (1958), CRAFTS (1960), and SZABO (1963). SUNDSTROM *et al.* (1979) cited detection of the 2-butoxyethyl ester of three different dichlorophenoxy isomers as evidence of the photochemical degradation of the 2,4,5-T.

CHENEY *et al.* [not dated] reported 2,4,5-T ester residue levels decreased rapidly on foliage of *Ceanothus* sp. after aerial application of 3.36 kg/ha as PGBE ester (Tables IV and V). They noted a 98% reduction in the level of ester and a 61% reduction in the level of acid the

Table V. *Levels of 2,4,5-T on foliage of Ceanothus sp. after aerial application of 3.36 kg/ha 2,4,5-T as PGBE ester.*[a]

Time after application (days)	Concentration of 2,4,5-T (mg/kg)	
	Ester	Acid
0[b]	132	15
1	142	12
3	90	5.1
8	51	4.1
15	6.3	4.2
21	3.0	1.8
32	2.7	5.8
228	<0.04	0.9

[a] CHENEY *et al.* [not dated].

[b] Immediately after spray.

first 30 days after application. The rapid loss of ester did not appear to be matched by a corresponding rise in the level of acid. These results suggest that while hydrolysis is certainly occurring, other processes (such as volatilization) may also be responsible for loss of the ester from the plant. Their finding of residues in air for several days after the application is consistent with this hypothesis.

Studies of 2,4,5-T residues in raspberry fruits in European forests have provided peculiar data. Based on reports by OLBERG (1973) and OLBERG *et al.* (1974), it appears that 2,4,5-T (6 kg in 250 L of water/ha in June and July) caused relatively fast leaf-wilt, but green berries continued to ripen and became "conspicuously large and beautiful." The results of residue analysis present a confusing picture. Initial residue levels were markedly different in the 2 yr of the study. First-year results with one formulation show a four-fold decrease in residue level in 41 days but virtually no change in residue level over the same period with a second formulation. The second year, initial residue levels were higher than the first year by a substantial margin. These levels declined relatively fast, however, with a mean half-life of 8.6 days for the first 15 to 17 days after treatment. There was a marked reduction in the rate of decrease after that time (Table IV). Residue levels varied from 0.4 to 2.2 mg/kg by the end of the measurement period, which ranged from 29 to 41 days on different plots. These levels are substantially greater than the 0.05 mg/kg residue level permitted in Germany. The results are confounded to some degree by apparent 2,4,5-T residues in untreated fruits. One control set had no detectable 2,4,5-T, but the other three contained residues ranging from 0.14 to 016 mg/kg (3- to 12-times greater than the permissible limit).

The successful development of the fruit after application makes one wonder about the overall effectiveness of the treatment. Some modification of formulation, carrier, or technique of application might accomplish more complete early season control such that treated fruits do not ripen. As a result of these studies, the season of application of 2,4,5-T in German forests was restricted to the period before fruit-set or after fruit harvest.

SILTANEN and ROSENBERG (1978) and MUKULA *et al.* (1975 and 1978) analyzed for residues in lingonberry, wild mushrooms, and aspen foliage from northeastern Finland after aerial application of 2,4-D and 2,4,5-T (2.5 kg/ha). The samples were collected at various periods from 2 to 52 wk after application. In lingonberries, residues of 2,4-D varied from <0.1 to 5.6 mg/kg and 2,4,5-T from 0.06 to 15 mg/kg at intervals up to 13 wk after application. Residues were not detected 1 yr later (2,4-D <0.05 mg/kg, 2,4,5-T <0.02 mg/kg) in fruits from plants which had survived the previous year's spraying. Wild mushrooms contained <0.05 to 1.2 mg/kg of 2,4-D and <0.02 to 1.8 mg/kg of 2,4,5-T at intervals up to 8 wk after application. In leaves and twigs of aspen, residues varied from 0.1 to 30 mg/kg of 2,4-D and 0.2 to 30 mg/kg of 2,4,5-T at intervals up to 3 mon after application. Similar values are reported for birch. In lingonberry plants killed by the spray, herbicide residues were still present (3 to 14.5 mg/kg of 2,4-D and 5.5 to 5.7 mg/kg of 2,4,5-T) in dead leaves and twigs 1 yr after application. These findings agree with those of PLUMB *et al.* (1977).

RAATIKAINEN *et al.* (1979) reported on residue levels of 2,4-D, 2,4,5-T, and MCPA in fruits of cowberry (*Vaccinium vitis-idaea*) at 35 days and bilberry (*V. myrtillus*) at 29 days after ground application of ester formulation of the herbicides at rates of 0.25, 0.75, and 2.25 kg/ha active ingredient. The residue levels were quite similar among compounds and between species, and there was an almost straightline correlation between the rate of application and the residue level (Table IV). The general level of the residues was of the same order of magnitude reported by MUKULA *et al.* (1978) for a similar study involving aerial application.

EICHLER and LEBER (1975) looked for residues of 2,4,5-T in honey, wild raspberry and blackberry fruits, wild raspberry leaves, and grass after ground application (backpack sprayer) of 6 kg/ha of 2,4,5-T in water in late July. Residues on vegetation declined more than 90% in 2 wk (Table IV). After 1 wk the fruit had lost its turgidity and was no longer considered desirable for picking. Jelly prepared from these fruits contained 1.8 mg/kg of 2,4,5-T: a 75 to 80% decrease in concentration in comparison to the initial concentration in the fresh fruit. WELLENSTEIN (1975 b) reported 4.15 mg/kg of 2,4,5-T in blackberry fruits 1 wk after helicopter application of herbicide (rate of application not specified). In marked contrast, MUKULA *et al.* (1978) found no difference in the residue level of 2,4-D or 2,4,5-T between raw lingonberries and jam prepared from the same fruits (about 2.1 mg/kg of each herbicide). Analysis of honey collected from a hive in the treated area and from another hive 50 m from the area 10 days after aerial application of 2,4,5-T ester showed no detectable (<0.005 mg/kg) 2,4,5-T (EICHLER and LEBER 1975). These findings agree with those of OLBERG *et al.* (1974), but WELLENSTEIN *et al.* (1975) reported 2,4,5-T at 0.006 to 0.009 mg/kg in bee honey.

ERNE and HARTMANN (1973) detected phenoxy herbicides at 4.4 mg/kg in lingonberries, 3.8 mg/kg in bilberries, 1.5 mg/kg in raspberries, and 4.5 mg/kg in mushrooms 4 days after application of herbicide at 2 kg/ha. After 1 mon, the residues were 2.9, 2, 1, and 0.4 mg/kg, respectively. Rinsing was not effective in reducing residues in lingonberries but removed up to 25% of the residues from mushrooms. Parboiling reduced residues by an additional 35%. Residues were not found in commercial lingonberry jam or berries.

Residues of MCPA were determined at different levels of the forest in a study area in northern Finland by ERONEN *et al.* (1979). Samples were collected at 0, 15, 40, 261, 283, and 297 days after aerial application of MCPA isooctyl ester (2.5 kg/ha). MCPA decreased 66% in birch twigs and foliage and 77% in mosses in the first 15 days after application (Table IV). Residues in moss decreased to 3 mg/kg in 40 days and were not detected 283 days after application. The rate of decrease was slower in the birch with 132 mg/kg detected at 40 days and 32 mg/kg still present at 283 days. These values are consistent with the values for 2,4-D and 2,4,5-T in birch and aspen reported by SILTANEN and ROSENBERG (1978).

ELIASSON (1973) provided valuable data on 2,4-D residues in foliage of young aspen treated with butoxyethyl ester in diesel oil as a basal treatment or with water-soluble amine in an injection treatment. Basal spraying resulted in much lower concentration of herbicide in foliage than did the injection treatment (Table VI).

BRADY (1973) did not present actual residue levels but did report 2,4,5-T had a half-life of 5.5 wk in loblolly pine (foliage, presumably) (*Pinus taeda*), 6.7 wk in sweet gum (*Liquidambar styraciflua*), 5.8 wk in post oak, and 12.4 wk in red maple (*Acer rubrum*). Slightly less than 2 wk were required for the loss of half the herbicide in the soil. He also

Table VI. *2,4-D residues in foliage from different parts of the crown of basal-sprayed or stem-injected aspen* (ELIASSON 1973).

Treatment	Crown part	Days after treatment 5 (mg/kg)	 28 (mg/kg)	 91 (mg/kg)
Basal spray	upper	20	12	20
	middle	10	5	4
	lower	0.2	0.3	0.2
Stem injection	upper	300	250	20
	middle	200	150	80
	lower	14	25	4

noted 97 to 99% of the initial dose remained in the treated foliage. NORRIS and FREED (1966 a and b) also found most of the applied dose remained in treated foliage in a glasshouse experiment. They reported 21 and 16% absorption of 2,4-D and 2,4,5-T as 2-ethylhexyl esters by foliage of bigleaf maple (*Acer macrophyllum*). About 95% of absorbed herbicide was still in the treated leaves 72 hr after application, and 94% of both herbicides was unchanged structurally in 7 days. Clearly, phenoxy herbicide in and on treated foliage is a potential major source of residues for the forest floor.

c) Behavior in forest floor and soil

Phenoxy herbicides reach the forest floor during application or later due to the washing action of rain or as residues in and on leaves that fall from treated plants.

1. Transfer to the forest floor.—In a computer simulation of 2,4,5-T behavior, WEBB *et al.* (1975) reported that rainfall can play an important role in moving herbicide residues to the forest floor. Their model used data for 2,4,5-T washed from red alder (*Alnus rubra*) foliage by artificial rain in a greenhouse study. This study showed rain applied 2 days after low-volatile ester of 2,4-D and 2,4,5-T resulted in washoff of 11 and 12% of the applied herbicide, respectively. Rain applied 9 days after treatment, however, removed only 3.3 and 7.5% of the applied 2,4-D and 2,4,5-T, respectively.

NORRIS *et al.* (1977) found a slight increase in the amount of 2,4,5-T in forest floor material between the time of application and 1 mon post-treatment in an Oregon forest in the spring. They attributed the increase to the washing action of rain on overstory vegetation. Rain is cited as an important factor in reducing plant herbicide residue levels (presumably by washing residues from the leaf surfaces to the ground) in studies with range grass (MORTON *et al.* 1967, BOVEY and BAUR 1972), in the forest (ERONEN *et al.* 1979), and in model ecosystems (VIRTANEN *et al.* 1979). ELIASSON (1973) tested the effect of rain (and other associated environmental parameters) on 2,4-D residue levels on leaves of young aspen plants treated with large quantities of 2,4-D butoxyethyl ester. Residues of 800, 100, and 20 mg/kg of 2,4-D were found on the leaves 11, 74, and 325 days, respectively, after treatment. Plants treated in the same manner but protected from the rain had 2,4-D residues of 2,000, 1,000, and 900 mg/kg at these same times.

NORRIS *et al.* (1978) measured the transfer of 2,4,5-T from the forest canopy to the forest floor in West Virginia. Throughfall precipitation contained detectable amounts of 2,4,5-T for 8 mon after aerial application (2.24 kg/ha ae as butoxyethyl ester) and deposited about 34 mg/m^2 of 2,4,5-T in the forest floor. More than 85% of the transfer occurred the first 20 days after application (99% in 5 mon). Only 6.0 mg/m^2 were transferred in fresh-fall litter the first year and 0.02 mg/m^2 the second year after application. At this site, a total of 71.3 mg/m^2 2,4,5-T entered the forest floor the first year after application (31.3 mg/m^2 during application, 34 mg/m^2 in throughfall precipitation, and 6 mg/m^2 in fresh-fall litter).

2. Movement and persistence in the forest floor and soil.—Phenoxy herbicide residues in the forest floor and soil are subject to volatilization, adsorption, leaching, uptake by plants, and a variety of chemical and biological degradation processes. These same processes operate in the agricultural environment but at different rates. Most studies in the forest, or using substrates from the forest, only examine reductions in herbicide residue levels with time and do not determine quantitatively the importance of particular residue reduction processes.

NORRIS (1966 and 1970 a) and NORRIS and GREINER (1967) reported a series of laboratory studies of the persistence of 2,4-D and 2,4,5-T in forest floor material (L, F, and H horizons) from a red alder stand. Using carboxyl ^{14}C-labelled 2,4-D and 2,4,5-T (2.24 kg/ha ae as triethanolamine salts in water), NORRIS (1966) found more rapid $^{14}CO_2$ release from 2,4-D- than from 2,4,5-T-treated forest floor material (89% for 2,4-D vs. 23% for 2,4,5-T in 315 hr). NORRIS and GREINER (1967) applied 2,4-D at 3.36 kg/ha to forest floor material from 5 different types of forest vegetation and determined herbicide persistence at intervals for 15 days (Fig. 1). They found statistically significant (but unimportant) differences in 2,4-D persistence among different types of forest floor material. They examined the influence of formulation on persistence and found a purified 2,4-D acid and laboratory-prepared (purified) 2,4-D triethanolamine salt were more readily degraded than commercial isooctyl ester or solubilized acid formulations (Fig. 1). The most striking difference was between the purified and the solubilized 2,4-D acids (the 2,4-D is in exactly the same chemical form in these two formulations). The slower rate of degradation of the solubilized acid was attributed to constituents of formulation which suggests one chemical can affect the rate of degradation of another. In a further examination of this point, they applied 2,4-D isooctyl ester at 3.36 kg/ha ae alone and with diesel oil at 37.4 L/ha or with DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] at 1.12 kg/ha. Diesel oil had no effect on the degradation rate of 2,4-D, but a slight stimulation of 2,4-D degradation was noted in the presence of DDT.

NORRIS (1970 a) examined in more detail the effects of various insecticides and herbicides on the degradation of 2,4-D and 2,4,5-T in red alder forest floor material. The results of this study are in Table VII. The percent recovery of 2,4-D and 2,4,5-T applied at two rates was the same, *i.e.*, the half-life is independent of starting concentration which suggests the rate of degradation follows first-order kinetics. Picloram and 2,4,5-T may cause an initial slowing of the 2,4-D degradation rate, but these differences were gone by the 35th day. The persistence characteristics of 2,4-D in the field probably will not be greatly altered by the simultaneous application of either 2,4,5-T or picloram.

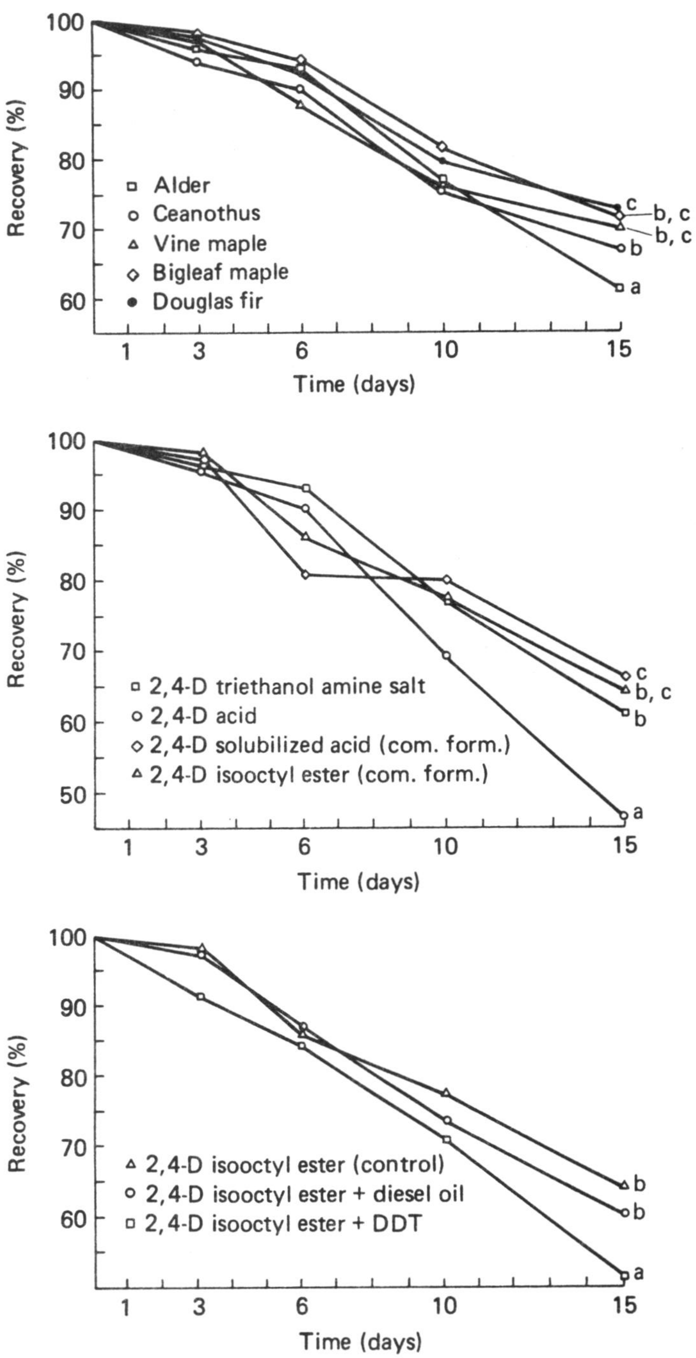

Fig. 1. Recovery of 2,4-D from forest floor material (Norris and Greiner 1967): top = effect of type of forest floor, middle = effect of formulation in red alder forest floor, and bottom = effect of diesel oil and DDT in red alder forest floor.

Table VII. *Recovery of 2,4-D and 2,4,5-T from red alder forest floor material* (Norris 1970 a).

Treatment	Recovery of herbicide (%) at		
	10 days	20 days	35 days
2,4-D (2.24 kg/ha)	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) 1 mon after DDT (1.12 kg/ha)	45	19	9
2,4-D (2.24 kg/ha) 1 mon after phosphamidon (1.68 kg/ha)	55	20	6
2,4-D (2.24 kg/ha) 1 mon after carbaryl (2.24 kg/ha)	51	15	11
	20 days	60 days	120 days
2,4,5-T (2.24 kg/ha)	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

In another test, the forest floor was pretreated with a representative from one of three classes of insecticide: an organochlorine compound, DDT; a carbamate, carbaryl (1-napthyl-*N*-methylcarbamate); and an organophosphate, phosphamidon (2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethylphosphate). 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. The small reduction in 2,4-D degradation (after application of carbaryl) is probably not important in field use. Thus, it appears the potential for alteration of 2,4-D persistence when applied to areas previously treated with 1 of these 3 insecticides is small. This relationship is also probably true for many other specific members of the organochlorine, carbamate, or organophosphate classes of insecticides and can likely be extended to the other phenoxy herbicides as well.

The rate of degradation of 2,4,5-T was accelerated by the presence of 2,4-D up to 60 days after application, but after 4 mon, recovery was the same as from forest floor material receiving 2,4,5-T alone. These various tests indicate that while it is possible for one chemical to influence degradation rate of another, the magnitude to which this occurs is not likely to result in important changes in the persistence of the phenoxy herbicides as they are used in the field.

In a laboratory study, Altom and Stritzke (1973) studied the degradation rates of 2,4-D, dichlorprop, 2,4,5-T, and silvex in a mixture of soil and litter from two forest sites and one grassland site in Oklahoma. The phenoxy herbicides were applied as diethanol amine salts in water to achieve a concentration of approximately 4.8 mg/kg ae in the soil-litter mixture. The degradation of 2,4-D was rapid in all soils with approximately 0.1 mg/kg remaining 20 days after application. Degradation of dichlorprop was not as rapid, and average residue levels for the 3 types of soil were 0.46 mg/kg at 20 days and 0.21 mg/kg at 40 days after application. Using average data for the 3 types of soil, 2,4,5-T and silvex showed a similar relative rate of degradation with 2.03 mg/kg remaining at 20 days and 1.05 mg/kg at 40 days. Silvex residues were 1.12 mg/kg and 0.6 mg/kg at these same times (Table VIII).

FOSTER and MCKERCHEN (1973) incubated 2,4-D, MCPA, and 2,4,5-T in several Saskatchewan soils in the laboratory. The reported half-lives varied from 14 to 41 days for 2,4-D and 1 to 2 days longer for MCPA. The half-life of 2,4,5-T was more than twice as long. SMITH (1978) in a similar study added phenoxy herbicides to a prairie soil to achieve 2 ppm concentration and then incubated the soil at 85% field capacity and 20°C in the laboratory. Degradation was rapid in all soils, and the average half-lives for 2,4-D, 2,4-DB, dichlorprop, 2,4,5-T, and silvex were <7, 7, 10, 12, and 12 days, respectively.

Phenoxy herbicides are frequently applied as esters (which have substantially different properties than the acid). The rate of ester hydrolysis to the acid is important in determining the behavior of the herbicide in the soil. SMITH (1972 and 1976) reported rapid hydrolysis of several esters of various phenoxy herbicides. Generally the rate of ester hydrolysis decreased with decreasing soil moisture and with increasing weight of the alcohol moiety. In soils at the wilting point, 90 to 100% hydrolysis of isopropyl, *n*-butyl, and isooctyl esters of 2,4-D occurred in 24 to 48 hr. The same results were found with esters of 2,4,5-T, dichlorprop, and 2,4-DB. BURCAR *et al.* (1966) reported complete disappearance of the isooctyl ester of 2,4-D in the soil (in Colorado) 14 days after aerial application at 2.24 kg/ha. In a laboratory phase of the study, the half-life of the ester was 0.63 day, but there was no corresponding increase in the acid, suggesting hydrolysis was not the only process of ester disappearance. STARK and TORSTENSSON (1978) indicated 2,4-D butoxyethyl ester required at least 1 mon for hydrolysis in Swedish forest soils and that the "acid" form of herbicide persisted for periods ranging from 2 mon in central Sweden to more than 9 mon in the north. STEWART and GAUL (1977) reported the isooctyl esters of 2,4-D and 2,4,5-T were not detected in soil 13 hr after application of 1.1 to 4.3 kg/ha of herbicide. At rates of

Table VIII. *Half-lives of herbicide in 3 soils* (ALTOM and STRITZKE 1973).

	Quachita Highlands		Cross-timbers
Herbicide	Forest (days)	Grassland (days)	Forest (days)
2,4-D	5	4	4
Dichlorprop	12	8	10
2,4,5-T	24	14	21
Silvex	21	14	15

application of 31 kg/ha, a small percentage of the ester persisted for several wk in soil. The major soil residues resulting were the respective free phenoxy acids which in turn decreased with time. CHENEY *et al.* [not dated] looked for both acid and ester forms of 2,4,5-T after aerial application of 3.36 kg/ha of 2,4,5-T as PGBE ester. They reported a rapid decline in the level of ester in the soil (9.2 mg/kg immediately after spraying, 1.6 mg/kg 3 days later and <0.04 mg/kg in 32 days) but no concomitant increase in the acid form. These data suggest that what has been assumed by some investigators to be ester hydrolysis is in fact loss due to volatilization, photochemical degradation, or some other process.

In a field study, ALTOM and STRITZKE (1972) reported dichlorprop and 2,4-D were completely dissipated from soil beneath a blackjack oak and post oak forests in 30 days, while 2,4,5-T residues persisted from 60 to 90 days. STEWART and GAUL (1977) found the maximum soil residues of 2,4-D and 2,4,5-T acid occurred at 14 to 22 days after application of isooctyl ester. The length of persistence varied with the rate of application, and 2,4,5-T residues were more persistent than 2,4-D residues at all application rates. The residues of both herbicides were found primarily at depths of zero to ten cm. With both herbicides, more than 90% of the applied chemical had disappeared within 70 days, and after 55 wk, residue levels were 0.1% of the initial application or less. In no case were residues found deeper than 20 cm after 55 wks. In a limited monitoring study in Minnesota, 2,4-D residues in the zero- to 7.5-cm soil zone decreased about 90% in 31 days after aerial application (1 mg/kg at 3 days, 0.94 mg/kg at 18 days, and 0.11 mg/kg at 31 days after application) (*U.S. Department of Agriculture, Forest Service* 1978 a). There was no significant leaching of 2,4-D below 7.5 cm in the soil.

PLUMB *et al.* (1977) reported on the persistence characteristics of 2,4-D and 2,4,5-T applied at 4.48 kg/ha ae each in 186 L of water/ha to a chamise site in southern California. Residue levels were not measured immediately after application, but both 2,4-D and 2,4,5-T showed a half-life of about 19 days for the period 14 to 29 days after application. Clearly, the rate of degradation changed with time (Table IX). Approximately 1 yr after application, residues for both herbicides were 0.04 to 0.05 mg/kg.

Table IX. *Average concentration of herbicide in soil from a chamise site in southern California* (PLUMB *et al.* 1977).

Days after treatment	2,4-D (mg/kg) at soil depth (cm)			2,4,5-T (mg/kg) at soil depth (cm)		
	0–10	10–20	20–30	0–10	10–20	20–30
14	1.16	0.16	0.09	0.88	0.06	0.03
29	0.71	0.07	0.05	0.53	0.02	0.02
69	0.22	0.02	0.02	0.29	0.01	0.03
146	0.11	0.02	0.01	0.21	0.02	0.01
379	0.04	0.02	0.02	0.05	0.03	0.03

The relatively rapid initial dissipation of both herbicides in the zero- to ten-cm soil zone is somewhat surprising. The low organic matter content, the texture of the soil, and the extremely dry conditions encountered during the first 5 mon after application do not favor microbial activity which is most often reported to be the responsible agent for phenoxy herbicide dissipation. Volatilization and photodecomposition may have been important processes in residue reduction at this site. BOVEY and BAUR (1972) suggested herbicide loss can be partially attributed to photodegradation and volatilization. Herbicide residues detected by PLUMB *et al.* (1977) in soil zones below ten cm are believed to be due to contamination during sampling of the dry, loose soil in the upper soil zones. Lack of rainfall for the first 29 days after application precludes leaching for this period.

At a grassland study site in Texas, BOVEY and BAUR (1972) found a rapid reduction in 2,4,5-T residue levels with time after application. Average initial herbicide residues for 5 different sites receiving 1.12 kg/ha was 4.23 mg/kg in the zero- to 15-cm soil zone. Six weeks after application these residue levels had declined to 0.03 mg/kg. There was little or no leaching of 2,4,5-T at the 5 study sites despite 13 to 45 cm precipitation within the first 12 wk of application. SCIFRES *et al.* (1977) reported residues of 2,4,5-T in the zero- to 2.5-cm zone declined to trace levels 28 days after application of 2,4,5-T and picloram (1.12 kg/ha each) at 3 range sites in Texas.

NORRIS *et al.* (1977) determined 2,4,5-T residues in forest floor and soil after 2 successive annual applications (2.24 kg/ha ae isooctyl ester in diesel oil by helicopter in March). The study area was a cool, moist site in western Oregon (Table X). The rate of decline in 2,4,5-T levels in forest floor after the first application at this site was slower than at the hot, dry site in southern California (PLUMB *et al.* 1977), which may reflect the importance of volatilization and photodecomposition on the loss of phenoxy herbicides from exposed soil surfaces. The rate of loss of 2,4,5-T was quite rapid the first 30 days after the second application, which indicates good adaptation of the microorganisms after the first application. One year after application, residue levels in forest floor were about 0.75% of the amount of herbicide originally applied.

In West Virginia, 2,4,5-T dissipated rapidly in the forest floor, despite substantial inputs in throughfall precipitation which occurred during the first 8 mon after application (NORRIS *et al.* 1978). At 1 wk, 52% of the level measured immediately after application still remained. At 3 mon 26% and at 12 mon 6% remained (Table X). These data show 2,4,5-T rapidly disappears from a variety of forest sites. There was some leaching of 2,4,5-T from the forest floor into the top 15 cm of soil, but movement into deeper soil zones did not occur (Table X) after the first application at either the Oregon or the West Virginia study sites. A similar pattern occurred after the second application at the Oregon site.

In Finland, ERONEN *et al.* (1979) found MCPA persisted for longer

Table X. *2,4,5-T in forest floor and soil after aerial application of 2.24 kg/ha 2,4,5-T ae in Oregon and West Virginia.*[a]

Residue location	Months after application 0	1	3	6	12	24
	First application—Oregon					
Forest floor (mg/m^2)	35.7	40.6	12.1	3.9	1.7	0.7
Soil (mg/kg)						
0–15 cm	0.01	0.02	0.08	0.02	0[b]	0
15–30 cm	0	0	0	0	0	0
30–45 cm	0	0	0	0	0	0
45–60 cm	0	0	0	0	0	0
	First application—West Virginia					
Forest floor (mg/m^2)	93.9	40.8	24.3	19.3	5.9	4.7
Soil (mg/kg)						
0–15 cm	0.34	0.03	0.03	0.02	0.03	0.01
15–30 cm	0	0.01	0	0	0	0
	Second application—Oregon					
Forest floor (mg/m^2)	137.4	9.7	12.5	4.1	1.5	—[c]
Soil (mg/kg)						
0–15 cm	0.01	0	0	0	0	—
15–30 cm	0	0	0	0	0	—
30–45 cm	0	0	0	0	0	—
45–60 cm	0	0	0	0	0	—

[a] Oregon data from NORRIS *et al.* (1977), West Virginia data from NORRIS *et al.* (1978).
[b] 0 means less than 0.01 mg/kg in soil or 0.1 mg/m^2 in forest floor.
[c] No samples were collected 24 mon after the second application.

periods in forest floor than has been reported for other phenoxy herbicides in the U.S. Unfortunately the data are expressed on a concentration basis (both fresh and dry wt) so allowances for variation in depth of forest floor among sampling locations is not possible. The values reported (dry-wt basis) are 112 mg/kg at 40 days, 95 mg/kg at 261 days, and 12 mg/kg at 283 days after application (2.5 kg/ha of MCPA isooctyl ester). In the soil which presumably was overlain by the forest floor, MCPA residues (dry-wt basis) were not detected immediately after application nor at depths greater than 3 cm more than 40 days after application. At 15 days, the residues were 4.0 mg/kg (0 to 3 cm), 0.3 mg/kg (3 to 6 cm), and 0.1 mg/kg (6 to 15 cm). Residues were as follows in the zero- to 3-cm zone of soil: 4.0 mg/kg at 15 days, 1.1 mg/kg at 40 days, 0.2 mg/kg at 283 days, and 0.7 mg/kg at 297 days.

In laboratory studies NORRIS (1970 b) found that the phenoxy herbicides were rapidly adsorbed by forest floor material, but the rate of desorption was also quite rapid, suggesting a low energy of adsorption and relatively good mobility in forest floor material with abundant rainfall. In the field, on the other hand, most studies showed relatively little leaching of phenoxy herbicides. Data in Table X suggest less movement of 2,4,5-T into soil from forest floor after the second application at the Oregon site, despite the fact that initial herbicide residue levels in the forest floor are nearly 4 times higher. This is accounted for by the rapid reduction of residue levels in the forest floor after the second application (probably from good microbial adaptation for 2,4,5-T degradation in soil after the first application). The initial rate of disappearance of 2,4,5-T in soil in West Virginia was rapid, but the rate slowed appreciably after the first mon.

d) Behavior in water

Phenoxy herbicides can enter surface water by direct application to stream surface, accidental drift from nearby treatment units, mobilization (during wet periods) of herbicide deposited in dry, ephemeral stream channels, overland flow during periods of intense precipitation, or leaching through the soil profile. The magnitude and duration of surface water contamination which might occur (and therefore organism exposure) from each of these processes is different. Direct application or drift to surface waters is likely to result in the highest concentrations of herbicide in the water, but the duration of entry is short, being largely restricted to the period of application. Therefore, organism exposure may be relatively intense, but brief. Mobilization of residues in ephemeral stream channels will occur only during the first few periods of heavy precipitation after application. Residue levels may be initially high but will decrease rapidly as stream levels rise and as residues are washed away. Organism exposure may resemble that resulting from direct application or drift.

Leaching and surface runoff are two competing mechanisms which move chemicals from spray deposits to streams. Most rainfall reaching the ground either enters the soil or flows over its surface. In both cases, surface-deposited chemicals are carried along either in solution or adsorbed on suspended matter. The nature of the surface and of the precipitation are the factors which influence the distribution of water between surface flow and infiltration. More specifically, these include (1) amount of surface organic matter, (2) slope, (3) depth of soil profile, (4) infiltration characteristics of soil, (5) intensity, duration, and form of precipitation, and (6) immediate previous precipitation history. Factors favoring infiltration will decrease the amount of surface runoff and with it the overland flow of chemical.

The amount of chemical actually entering a stream due to surface flow will be influenced by (1) distance from stream course to closest point of chemical application, (2) infiltration properties of soil or surface organic matter, (3) rate of surface flow, and (4) adsorptive characteristics of surface materials. Conditions which retard the rate of surface runoff will minimize the immediate level of stream concentration and also reduce the long-term stream load of pesticide, because a longer residue time in the soil provides greater opportunity for adsorption and degradation.

If precipitation is sufficient to cause overland flow, stream discharge volumes are likely to be considerably greater than during periods of application, and therefore herbicide concentrations would probably be lower. The duration of entry via overland flow would be brief, being restricted to periods of particularly intense precipitation. If herbicides enter streams by leaching, the concentrations will be quite low, but the duration of entry could conceivably be considerably longer than for either direct application or the overland flow process. The role of each of these processes in relation to stream contamination from operational use of phenoxy herbicides in forestry are considered in the following sections.

1. Entry to streams via leaching.—On a relative scale, phenoxy herbicides are considerably more mobile in the soil than many pesticide materials, but in fact their movement is still quite small compared to the distance from treated areas to streams (HARRIS 1967 and 1969). Numerous investigators have shown herbicide persistence and mobility in the soil are inversely correlated with organic matter. Laboratory or agriculturally based studies by O'CONNOR and WIERENGA (1973), O'CONNER and ANDERSON (1974), EDWARDS and GLASS (1971), LUTZ *et al.* (1973), WIESE and DAVIS (1964), HELLING (1971 a, b, and c) and forest- and range-based studies by NORRIS *et al.* (1977), PLUMB *et al.* (1977), and BOVEY and BAUR (1972) all support the hypothesis that leaching of phenoxy herbicides is not an important process for transporting significant quantities of these chemicals to streams.

2. Entry to streams via overland flow.—This process requires overland flow of water, a phenomenon hydrologists report is relatively uncommon on most forest sites. The infiltration capacity of the forest floor and soil far exceeds most rates of precipitation. Infiltration capacities in excess of 100 cm/hr are not uncommon in many forest environments. Overland flow may occur in areas where soils are badly compacted, are water repellant, or have no surface protection in the form of forest floor or vegetation.

BARNETT *et al.* (1967) maximized the probability of runoff by applying artificial rain (6.25 cm/hr) to recently tilled agricultural land and found 38% of the 2,4-D isooctyl ester but only 5% of the 2,4-D amine salt in the washoff (mixture of eroded soil and water). The concentration of 2,4-D (isooctyl ester) in the washoff increased from 0.9 to 1.95 mg/L as the temperature of the artificial rain increased from 8° to 27°C (1 day after application). Equally, however, the concentration decreased most rapidly during the one-hr test rain when the rain was 27°C than when it was 8°C (estimated half-time was 18 min at 27°C and 65 min at 8°C).

NORRIS (1969) reported runoff of 2,4-D and picloram from a powerline right-of-way in southwestern Washington where there was evidence of soil compaction. The highest concentration of 2,4-D in runoff water (0.825

mg/L) was associated with the first significant storm after application. The concentration decreased with subsequent storm events even though those storms were larger than the first storm. No residues were found beyond about 6 wk after the first runoff event. TRICHELL *et al.* (1968), BOVEY *et al.* (1974), and SCIFRES *et al.* (1977) also reported research demonstrating runoff of herbicides from agricultural or rangeland situations.

Where runoff does occur, the concentration of herbicide in the transporting water may be reduced as it passes over unsprayed areas. ASMUSSEN *et al.* (1977) applied simulated rainfall 1 day after application of 0.56 kg/ha 2,4-D to plots planted with corn. The runoff from the plots was directed through a 24-m-long grassed waterway. Of the rainfall applied one day after application of herbicide, 50% ran off under dry antecedent soil conditions and 78% ran off under wet conditions. Reduction of suspended sediment in the waterway was 94 to 98% of the total amount of sediment moving from the plot. The total amount of 2,4-D moving from the plot was 2.5% and 10.3% in the dry and wet antecedent soil conditions. Of the 2,4-D lost in solution from the plot, about 70% was removed from solution as the runoff flowed over the 24-m grassed waterway. TRICHELL *et al.* (1968) also found substantial decrease in both the concentration and total discharge of picloram when the contaminated water ran over untreated soil.

Increased outflow of phenoxy herbicide from treated watersheds may occur with heavy rains, but the process is more likely to involve the mobilization of surface residues from streambanks and ephemeral stream channels rather than overland flow. Mobilization occurs as the stream network expands during precipitation. Research on this process is reported in the following section.

3. Direct application or drift to surface waters and mobilization in ephemeral stream channels.—Direct application and drift to surface water or ephemeral stream channels are the principal routes of phenoxy herbicide entry to forest streams, lakes, and ponds. These are also the processes over which the applicator and forest manager can have the greatest influence. Substantial research, operational, and regulatory experience has been gained in this area. PATRIC (1971) and NORRIS and MOORE (1971) provided useful compilations of some studies of herbicide entry to forest streams. The following paragraphs describe and discuss results of studies of research and monitoring for stream contamination in connection with the operational use of phenoxy herbicides in forest and range sites. Most of the residues detected in these studies resulted from direct application or drift to surface water or ephemeral stream channels. In those cases where monitoring continued for long periods, data related to leaching and overland flow are also included.

NORRIS (1967), reporting research done by Norris, Newton, Zavitkovski, and Freed, presented data on herbicide residues in streams from several watersheds in Oregon forests treated with 2,4-D, 2,4,5-T, or a combination of the 2 herbicides. All treatments were low-volatile esters in diesel oil or water applied by helicopter at rates ranging from 1.12 to 3.36 kg/ha ae. The results showed some herbicide was present in nearly every stream which passed through, or was adjacent to, treated areas.

Maximum concentrations ranging from 0.001 mg/L to 0.13 mg/L occurred during or shortly after application. The highest concentrations and longest persistence occurred when no provisions were made to avoid direct application to stream surfaces in the treated areas. The time required to return to nondetectable levels (<0.001 mg/L) varied with the nature of the area treated and the maximum herbicide concentration observed. Times ranging from less than 1 hr to more than 168 hr have been noted, with less than 1 day required in most instances.

In Alaska, SEARS and MEEHAN (1971) found no residues in stream water the first 2 days after application of 2.24 kg/ha ae 2,4-D butyl ester. On the third day after application, however, one sample contained 0.2 mg/L 2,4-D. A 30-m unsprayed buffer strip was left along the main part of the stream to minimize entry of herbicide to the stream, but no effort was made to avoid application to numerous small tributaries. They also noted that wind currents during the spray operation caused some deposit in the main stream despite the buffer strip.

NORRIS (1967) found herbicide applications to marshy areas (areas with a high water table) can lead to higher than normal levels of stream contamination. In one instance, concentrations approaching 1.0 mg/L of 2,4-D were found in water flowing from a marshy area. 2,4-D continued to flow from the area in detectable concentrations for the duration of a 168-hr sampling period. He noted, "This particular situation (treating marshy areas) is probably one of the most dangerous in terms of potential stream contamination since a very slight rise in the water table could result in the release of very large quantities of herbicide to streams draining such an area."

ALDHOUS (1967) used a thin-layer chromatographic system (reported sensitivity of 0.005 mg/L) to monitor 2,4-D in surface water in the bottoms of ploughed furrows in a peat area treated with nonyl ester of 2,4-D (applied by aircraft at 4.5 kg in 155 L of water/ha). High levels of herbicide (1.5 to 2.0 mg/L) were found for the first 7 days, but no detectable residues were found after 28 days. The author indicated these residues were the result of drainage water mobilizing 2,4-D residues originally deposited in the furrow bottoms (the same mechanism which operates in ephemeral stream channels). Stream contamination could result if substantial surface drainage from this type of area occurs (BARNETT *et al.* 1967).

NORRIS (1967 and 1968) looked for the long-term entry of 2,4-D and 2,4,5-T into forest streams draining areas receiving these herbicides. In one study, 11 streams in western Oregon were monitored immediately below treatment areas on a regular basis for 9 mon after application. Once the initial stream contamination had declined to nondetectable limits, no herbicide residues were detected during first fall rains or subsequent periods of heavy precipitation. In a second study, two other watersheds in western Oregon were studied. In one, the treatment area bordered a stream for more than 3 km and extended 200 to 400 m upslope. 2,4-D and 2,4,5-T were applied at 1.12 kg/ha ae each as low-volatile esters in diesel oil in the spring. The second area contained 25 different treatment areas totalling 160 ha which received the same treatment in a 1135-ha watershed. In both cases, streams were sampled to detect the movement of herbicide from treated areas to the stream during the first fall storms which raised stream levels. No residues were found.

Norris, Newton, Zavitkovski, and Freed (see NORRIS 1967) noted a rapid decrease in herbicide concentration with downstream movement. An estuary receiving water from a large forest area which included numerous herbicide treatment areas showed no detectable phenoxy herbicides (<0.001 mg/L). Through the use of buffer strips and careful attention to details of application, phenoxy herbicide concentrations in forest streams will seldom exceed 0.01 mg/L and will not persist for more than 24 hr. Public and private forest management groups in the Pacific Northwest have monitored streams for herbicide residues during and after operational brush control operations since the mid-1960s. The results of these efforts confirm the findings discussed above.

In southern California, KRAMMES and WILLETS (1964) sampled for 2,4-D and 2,4,5-T in a small stream after application to control riparian vegetation. Maximum concentration detected was 0.09 mg/L and residues were found in only 2 samples; however, the sampling intensity was not great.

In an Arkansas forest, LAWSON (1976) sampled stream water during a rising hydrograph to look for storm-induced herbicide runoff after treating two 0.6-ha watersheds with 4.48 kg/ha ae 2,4,5-T in diesel oil by backpack sprayer in 3 successive yr. The sampled streams were ephemeral, not perennial, and flowed only during significant storms. 2,4,5-T residues up to 2.2 mg/L were detected in water collected in connection with the first runoff event which occurred 17 days after application. Less than 0.2 mg/L of 2,4,5-T was detected in the perennial stream which received the ephemeral streamflow from this area. Barely detectable levels of 2,4,5-T were found in samples collected during the next runoff event, approximately 7 wk after application. Subsequent storms did not produce detectable 2,4,5-T residues. These residues appear to be the result of herbicide mobilization from stream channels which were dry at the time of treatment. No herbicide residues were detected in samples collected during runoff events after either the second or the third application. These latter results are difficult to interpret but may suggest decomposition of the herbicide by microbial populations adapted to the use of 2,4,5-T after the first application. In any case, it is clear that in this Arkansas forest significant movement of 2,4,5-T from treated areas to perennial streams did not occur.

In a similar forest type in Oklahoma, IGLEHEART *et al.* (1974) measured 2,4,5-T residues in water collected from streams immediately below 4 areas treated at a rate of 2.24 kg/ha ae as 2,4,5-T PGBE ester applied by helicopter in May and June. Treated areas ranged in size from 100 to 800 ha and constituted 20 to 100% of the watershed. The results were similar to those of NORRIS (1967). Maximum concentrations occurred shortly after application, and residues declined to low or nondetectable levels in a short time (Table XI). Maximum herbicide concentrations were quite similar to those in Pacific Northwest streams which originated in or ran directly through treated areas and where no effort was made to avoid direct application to stream surface. IGLEHEART *et al.* (1974) noted that the first significant rains did not introduce important quantities of 2,4,5-T into the streams.

SUFFLING *et al.* (1974) monitored for herbicide runoff in an Ontario forest for 1 yr after application of a 1:4 mixture of picloram:2,4-D (9.35 kg/ha ae) to a powerline right-of-way. The first runoff event took place the day of application, and 0.001 mg/L of 2,4-D was detected. This is the only time detectable levels of 2,4-D occurred at this site which again suggests mobilization of residues in ephemeral stream channels as the probable mechanism rather than overland flow.

REIGNER *et al.* (1968) used odor tests to look for phenoxy herbicides in Pennsylvania and New Jersey streams in 4 forest areas treated with butoxyethanol or emulsifiable acid formulations of 2,4,5-T applied by mist blower. About 0.04 mg/L of herbicide was detected immediately after application, but residue levels declined about 50% in 4 hr, and no residues were detected in samples collected at various intervals over the next 4 wk. Samples collected from the Pennsylvania streams in connection with the first storm to produce more than 2.5 cm precipitation contained

Table XI. *Herbicide in stream water from Oklahoma forests treated with 2.24 kg/ha of 2,4,5-T by helicopter* (IGLEHEART *et al.* 1974).

	Residue (mg/L)[a]			
Time after application	Site 1	Site 2	Site 3	Site 4
Prespray	0	0	0	0
1 hr	0.027	0.001	0	0
4 hr	0.145	0.018	0.023	0.031
1 day	0.010	0.011	0.005	0.002
7 days	0	0	0.002	0
14 days	0	0	0	0
30 days	0	0.002	0	0
After first significant rain	0	0.001	0.001	0

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[a] 0 means <0.001 mg/L.

0.01 and 0.02 mg of 2,4,5-T/L. The New Jersey streams did not contain detectable herbicide after a similar storm. This study is limited by the nonspecific detection method used.

In West Virginia NORRIS *et al.* (1978) studied the fate of 2,4,5-T in a 22-ha watershed aerially sprayed at 2.24 kg/ha ae of butoxyethanol ester. A maximum of 0.05 ppm of 2,4,5-T was found in stream water collected immediately below the treated areas about 3 hr after application (following a brief but intense rain shower of 1.3 cm the first hr after application) (Fig. 2). Residues were detected sporadically the first 11 days after application, with highest concentrations occurring during 3 rainy periods. No residues greater than 0.01 mg/L were detected more than 1 day after application. No residues (<0.001 mg/L) were found more than 11 days after application, although sampling continued for more than 2 yr. About 0.0175% of the 48 kg 2,4,5-T applied to this watershed was discharged in streamflow (NORRIS 1980). No residues were found at 2 downstream locations.

PIERCE (1969) applied 2,4,5-T and 5-bromo-3-*sec*-butyl-6-methyluracil (bromacil) by backpack sprayer to prevent revegetation on an experimental watershed in New Hampshire. Samples were collected for more than 1.5 yr, and the concentration of 2,4,5-T did not exceed 0.001 mg/L at any point although during this same period the concentration of bromacil was as high as 1.4 mg/L. The bromacil had been applied at 28 kg/ha by helicopter and, although the data are limited, it appears 20% of the bromacil left the watershed in streamflow within the first 1.5 yr after treatment.

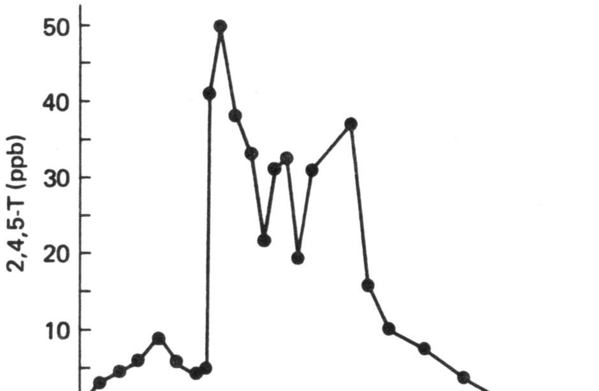

Fig. 2. Concentration of 2,4,5-T in a forest stream immediately downstream from a 22-ha watershed aerially sprayed with 2.24 kg/ha ae of butoxyethanol ester of 2,4,5-T, West Virginia (NORRIS *et al.* 1978).

In North Carolina, Douglass *et al.* (1969) applied 2,4-D and 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine (atrazine) with groundspray equipment to convert a hardwood stand to grass in an effort to increase water yield. In the first application only atrazine was applied and no buffer strip was left. Atrazine to 0.04 mg/L was detected in the stream with highest concentrations occurring during rainstorms a few days after application. In the second application a 3-m buffer strip was left between the stream channel and the area receiving 2,4-D (isobutyl ester at 3.36 kg/ha ae). No 2,4-D was found in the stream draining the 8-ha watershed even during several storms depositing more than 2 cm of rain/day in the first 2 mon after the second application. Edlund and Tangden (1977) reported only one sample out of 18 taken at 6 sites on 3 occasions showed any trace of phenoxy herbicide (<0.005 mg/L) after spraying (aerially) a test area (in Sweden) with MCPA or 2,4-D.

Limited scale monitoring of operational applications of phenoxy herbicides on forest lands is largely in agreement with the research reports cited in this section. Various reports of some of these efforts contain some data on residues of 2,4-D, silvex, and 2,4,5-T in water (*U.S. Department of Agriculture, Forest Service* 1978 a, b, and c). *U.S. Department of Agriculture, Forest Service* (1980) recently analyzed reports of the results of monitoring for phenoxy herbicides in streams after operational application in forests of the northwestern United States. The reports analyzed represented 680 samples from 304 different applications. In most cases, a composite sample was made from 2 to 5 individual samples. They found 84% of the samples did not contain herbicide residues, 14% had residues up to 0.005 mg/L, 1% had between 0.005 and 0.01 mg/L, and 1% contained more than 0.01 mg/L.

Hammerstrom *et al.* (1971) reported the results of a "one time sampling" survey of 58 community water supplies for 2,4-D, 2,4,5-T, and silvex. 2,4,5-T was detected in 11 or 19% of the water supplies at concentrations ranging from <0.0005 to 0.00057 mg/L. 2,4-D at levels of <0.0005 to 0.0034 mg/L was detected in 31% of the water supplies. Silvex was detected in 6.9% of the water supplies at concentrations of <0.0005 mg/L. Most of the water supplies sampled were downstream from agricultural or mixed agricultural and forestry areas. Most samples reported as positive for phenoxy herbicide were less than the quantitative level of detection (0.0005 mg/L). Of the 6 samples that contained more than 0.001 mg/L (all 2,4-D, no 2,4,5-T or silvex), 5 were from Oklahoma.

Brown and Nishioka (1967), Manigold and Schulze (1969), and Schulze *et al.* (1973) surveyed western U.S. streams for pesticides between 1965 and 1971. No phenoxy herbicides were found in any of the streams sampled by Brown and Nishioka (1967), but 2,4-D, 2,4,5-T, and silvex were detected in many streams by Manigold and Schulze (1969) and in every stream sampled (but not every sample collected) by Schulze *et al.* (1973). The maximum concentration detected was 0.00099 mg/L of 2,4-D. There was substantial variation from yr to yr and among locations. In nearly every case the sampled streams were in or received runoff from nearby agricultural lands.

These various studies and monitoring programs largely support the conclusion that direct application and drift to surface water and mobilization in ephemeral stream channels are the principal sources of phenoxy herbicides in forest waters. Overland flow and leaching do not appear to be important. Residues in water from direct application and drift can largely be controlled through careful orientation of spray units to streams and by careful attention to climatic, equipment, and application factors.

4. Fate in streams.—The fate of phenoxy herbicides in forest stream systems has received little direct study, although some inferences can be made from monitoring studies. NORRIS and MOORE (1971) presented some information on this point, but their inferences are largely based on studies done in the laboratory or in surface waters not particularly associated with forests. PARIS and LEWIS (1973) summarized the work reported in the literature between 1945 and 1971 concerning the photochemical, chemical, and microbial degradation of 10 selected pesticides, including 2,4-D butoxyethyl ester, in water. The processes which operate on the phenoxy herbicides in the terrestrial environment also operate in aquatic systems, but the rates are likely to be different.

Adsorption, uptake by organisms, volatilization, and downstream transport are processes which, while they do not eliminate phenoxy herbicides from the environment, reduce the exposure organisms in a particular area may receive. Degradation—microbial, chemical, or photochemical—is the only process which can reduce total environmental load. Widely divergent results have been obtained in studies of phenoxy herbicide behavior in the aquatic environment. Some of this divergence results because persistence reflects the combined result of numerous processes which change the level of herbicide in one area, and the rate at which any one process operates varies widely among areas.

a) Hydrolysis of phenoxy herbicide esters.—Phenoxy herbicide esters hydrolize in water at pH, temperature, and buffer conditions which are found in nature. The esters are more toxic than the acid or salt forms, thus rapid hydrolysis will substantially reduce the potential for toxic impacts on aquatic organisms. The half-lives for hydrolysis of various phenoxy esters varied from 4.5 to more than 88 days at pH 7.4 (Table XII); however, persistence of the acid forms (the products of hydrolysis) may be lengthy (STRUIF *et al.* 1975).

KENAGA (1974) (reporting the unpublished research of Teasley and Williams) showed that at concentrations of about 1 mg/L ae the following % hydrolysis of 2-ethylhexyl ester of 2,4,5-T occurred: 42% in 4 hr, 67% in 8 hr, and 88% in 16 hr. Ultraviolet light was an important factor in the hydrolysis of esters of both 2,4,5-T and silvex. ZEPP *et al.* (1975) used theoretical considerations (and some data) to calculate the half-lives of a series of 2,4-D esters. At pH 9.0, the half-lives were: methyl (1.1 hr),

Table XII. *Hydrolytic half-lives of phenoxyacetic acid esters in water at pH 7.4.*[a]

		Half-life (days) at	
Chemical	Phenoxyester	4°C	20°C
2,4-D	-methyl	44.7	4.5
	-*n*-butyl	—	5.0
	-isopropyl	—	23.1
2,4,5-T	-methyl	36.4	—
	-*n*-butyl	48.5	7.5
	-isobutyl	61.0	10.2
	-*n*-amyl	57.4	8.4
	-3-methylbutyl	88.2	11.6

[a] From Table 3 of STRUIF *et al.* (1975).

isopropyl (17.0 hr), *n*-butyl (5.2 hr), *n*-octyl (5.2 hr), and isooctyl (37.0 hr). At pH 6.0, the half-lives were longer: methyl (44 days), isopropyl (710 days), *n*-butyl and *n*-octyl (220 days), and isooctyl (1,500 days). Clearly, both biotic and photolytic factors are important in ester hydrolysis because persistence at near-neutral pH of the length calculated by ZEPP *et al.* (1975) does not seem to occur in natural conditions.

ALY and FAUST (1964) found 2,4-D esters were hydrolyzed to the acid form in 9 days in lake water. RODGERS and STALLING (1972) reported a half-life of about 24 hr for the BEE ester of 2,4-D. In a field test where 2,4,5-T (PGBE ester) was applied at 3.36 kg/ha, CHENEY *et al.* [not dated] reported the rapid hydrolysis of ester in the water of a trough that was directly sprayed. 2,4,5-T ester was highest (0.364 mg/L) 1 day after application; 2 days later no ester (<0.001 3 mg/L) was detected. The level of 2,4,5-T acid, however, had increased to a maximum level of 0.249 mg/L.

COCHRANE *et al.* (1967) reported the propylene glycol butyl ether ester of silvex was rapidly and almost totally hydrolyzed to silvex acid in about 2 wk when applied at about 9 kg/ha to water over 3 different loam, sand, or muck soils. Between 1 and 7 days after application, the concentration of ester decreased from about 0.3 to 0.01 mg/L, while the silvex acid levels increased from about 0.4 to 1.6 mg/L. Less than 0.001 mg/L of ester remained at the end of two wks.

BAILEY *et al.* (1970) reported 50% hydrolysis of the PGBE ester of silvex in treated ponds in 5 to 8 hr, 90% in 16 to 24 hr, and 99% in 33 to 49 hr. Both silvex ester and acid forms were found in the sediment, although surprisingly the ratio of acid to ester was about 10 in the sediment but about 0.1 in the water 4 hr after treatment. The ester had essentially disappeared in 5 wks.

β) *Adsorption of phenoxy herbicides.*—Phenoxy herbicide esters adsorb extensively to flocculated humic acids with the degree and strength of adsorption increasing with the number of carbon atoms in the alcohol moiety. At neutral pH and with slight humic acid content, STRUIF *et al.* (1975) reported phenoxy acids were not appreciably adsorbed, but the adsorption of various esters was extensive. A nearly linear, inverse relationship existed between the water solubility and the Freundlich adsorption equilibrium constant. In natural water systems, both adsorption and hydrolysis will occur at the same time. STRUIF *et al.* (1975) reported the rates of hydrolysis of several phenoxy herbicide esters were about twice as fast in aqueous systems that also contained humic acid. This indicates hydrolysis may be more rapid when the ester is adsorbed, a hypothesis consistent with the data of BAILEY *et al.* (1970) who reported a ratio of silvex acid to ester of 10 in pond sediments 4 hr after application of silvex ester.

COCHRANE *et al.* (1967) reported both the ester and acid forms of silvex were adsorbed by the hydrosoil, although the authors were uncertain that the ester per se was being adsorbed. In followup laboratory tests, they found rapid equilibration of silvex ester and acid between the water and sediment phases. After 16 hr of shaking, more than 90% of the ester was adsorbed (either as acid or ester) on 2 of the 3 soils tested. The acid was also extensively adsorbed (86 to 100%) in the same period.

BAILEY *et al.* (1970) reported both the acid and ester forms of silvex were found in sediment, but the adsorption of the ester was not as extensive as would have been predicted from the data of STRUIF *et al.* (1975). BAILEY *et al.* (1970) indicated the adsorptive capacity of the pond sediments was saturated when the concentration of herbicide in water exceeded 2 mg/L. The apparent limited adsorption capacity may be due to the limited sediment-water interface. In flowing streams with some suspended sediment component in the water column, more extensive adsorption may occur.

Aquatic plants will also absorb some phenoxy ester from water. SMITH and ISOM (1967) reported 8.26 mg/kg of 2,4-D (butoxyethanol ester) in eurasian watermilfoil (*Myriophyllum spicatum* L.) 24 hr after application of the granular herbicide at 112 kg/ha ae. The water concentration was 0.037 mg/L 8 hr after treatment and <0.001 mg/L at 24 hr. Residues of 2,4-D in sediment ranged from 0.14 to 56.8 mg/kg. SCHULTZ and WHITNEY (1974) studied the distribution and fate of 2,4-D (4.48 kg/ha as the dodecyl-tetradecyl amine salt) in a canal in Florida. The highest concentration of 2,4-D in the water was 0.037 mg/L the day after treatment; no sediment sample contained more than 0.005 mg/kg (detection limit) 2,4-D.

Clearly, phenoxy herbicides, either as acids, salts, or esters, will interact with stream sediments. The net effect of this interaction is to reduce the instantaneous concentration of the chemical in the water. The total length of time the herbicide will be in the water may be increased as desorption from sediments occurs; however, the total load of aquatic pollutant will be reduced as the biological and chemical processes of herbicide degradation occur while the herbicide is in the sediment. It is important, from the standpoint of evaluating toxic hazards to aquatic organisms and downstream water users to recognize and take into account the adsorption-desorption equilibrium which will develop between the water and sediment phases for all phenoxy herbicides in the aquatic environment (PIONKE and CHESTERS 1973).

γ) *Persistence of phenoxy herbicides.*—Phenoxy herbicides are also degraded (or disappear) from aquatic systems. SIKKA and OU (1976) and OU and SIKKA (1977) incubated silvex (300 mg/L) in a mixed culture of aquatic microorganisms developed by an enrichment technique from pond water and sediment. After 80 hr, essentially all the chlorine in the herbicide had been liberated as free chloride. Liberation of $^{14}CO_2$ from the ring-labeled silvex and loss of UV absorbance indicated ring cleavage had occurred. About 1 to 5% of the initial silvex was identified as trichlorophenol, which was also rapidly metabolized.

ROBSON (1966) reported 2,4-D degradad from 4.5 to $<$0.05 mg/L in fewer than 14 days in stagnant pond water. ROBSON (1968) also reported a marked decrease in 2,4-D persistence in fresh water (from 9 wks to 1 wk) when small quantities of soil previously treated with 2,4-D were added to the water. Presumably the soil contained its natural complement of microorganisms.

SONDERQUIST and CROSBY (1975) reported MCPA essentially disappeared from the water and sediment of a rice pond in California 14 days after application of 0.98 kg/ha of MCPA dimethylamine salt. Tests in other environments indicate persistence can be appreciable. SCHMIDT (1975) reported 100% of 2,4,5-T, 91% of MCPA, and 85% of 2,4-D were recovered 168 hr after their addition to water. ALY and FAUST (1964) reported 2,4-D persisted up to 120 days in lake water. In another study only 40% degradation of 2,4-D was observed in water in 6 mon under conditions that seemed excellent for biological activity (SCHWARTZ 1967). CHENEY *et al.* [no date] found highest residues of 2,4,5-T acid (0.249 mg/L) 3 days after aerial application of 2,4,5-T ester over a watering trough. The level of acid decreased erratically to 0.132 mg/L after 1 mon and 0.002 mg/L after 8.5 mon. In a pond treated with the BEE ester of 2,4-D, herbicide was no longer detected in water 36 days—and in hydrosoil 85 days—after treatment with 20% granules applied to achieve 1.33 mg/L of herbicide (FRANK and COMES 1967). COCHRANE *et al.* (1967) found rapid disappearance of silvex ester but longer persistence of silvex acid in water over sand, loam, or muck soils. Silvex acid decreased from 1.6 mg/L to about 0.05 mg/L in 18 wks.

DEMARCO *et al.* (1967) demonstrated the effect of temperature and level of oxygen in water on persistence of 2,4-D. They reported a considerable decrease in the rate of 2,4-D loss in biologically active natural river water at reduced levels of dissolved oxygen (Fig. 3). In a laboratory study CROSBY and WONG (1973) found the photodecomposition of 2,4-D

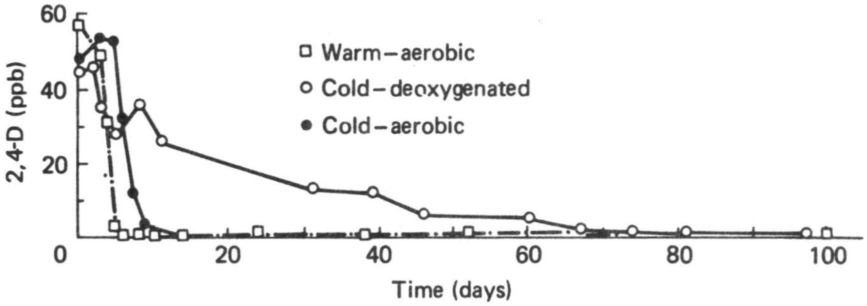

Fig. 3. The effect of temperature and oxygen level on persistence of 2,4-D in water (DEMARCO *et al.* 1967).

and 2,4,5-T was slow (half-life more than 1,800 hr). The authors felt photodecomposition may be more rapid in natural water. Rapid degradation of 2,4-D occured in water samples collected from areas with a history of repeated 2,4-D applications (GOERLITZ and LAMAR 1967). Some of these results may indicate some surface waters lack conditions suitable for biological activity or they may not contain populations of microbes adapted to the use of the phenoxy herbicides as substrates (HEMMETT and FAUST 1969).

AVERITT and GANGSTAD (1976) studied the rate of dissipation of 2,4-D at the point of application to waters for aquatic vegetation control. The results showed the rate of dissipation depended on the dosage rate, depth of water, mean temperature, and time since treatment. For application to the water surface of 4.48 kg/ha, there was a decrease of 0.058 mg/L for each 0.61-m increase in depth of water treated, 0.115 mg/L for each 7°C increase in temperature, and 0.053 mg/L for each 7 days after treatment.

The wide range of results presented in this section indicate the persistence of phenoxy herbicides in aquatic systems is influenced by many factors. The influences of environmental factors on the rates of clearance of 2,4-D and its derivatives from water are summarized in Table XIII.

5. Stream loading.—Most of the research on herbicides in the aquatic environment have only measured the concentration of chemical in the water. Without measurements of stream discharge for the same time period, it is not possible to estimate stream loading with any accuracy. NORRIS *et al.* (1976 c and 1981) have reported one of the few such studies done in the forest. They measured the discharge of herbicide in stream water from a 7-ha watershed in southwestern Oregon after aerial application of 2.3 kg/ha of picloram and 4.6 kg/ha of 2,4-D in June. The stream was intermittent and flowed only between November and May and during periods of heavy precipitation in late spring and early fall. About 0.022 ppm of 2,4-D was detected in the first outflow from the watershed which occurred in October, about 3.5 mon after application. The last detectable level of 2,4-D (0.003 ppm) was found in samples collected 12 days later. Despite heavy rains and high rates of stream-water discharge from this watershed, no further outflow of 2,4-D was detected in samplings made over the next 2 yr. Of the 32.2 kg 2,4-D applied to the watershed, 4.5 g (0.014%) was discharged in stream water. The intermittent stream channel occupied 0.21% of the area of the watershed which suggests that residues detected represented mobilization of residues in the channel rather than either overland or subsurface flow. In West Virginia, NORRIS (1980) found 0.0175% of the 2,4,5-T applied to a 22-ha watershed was discharged in streamflow. All the discharge occurred in the first 11 days after application, although sampling continued for more than 2 yr.

FRANK and RIPLEY (1977) and FRANK *et al.* (1978) reported on the stream loading of 2,4-D, 2,4,5-T, and MCPA in 11 small agricultural watersheds in Ontario, Canada (Table XIV). While this is hardly the "forest environment," this study is unique in its scope, and the data are consistent with those reported by NORRIS *et al.* (1981) for 2,4-D and picloram and NORRIS *et al.* (1976 b) for trichlopyr.

SHEETS *et al.* (1972) reported on herbicide residues in surface runoff and flume water at the base of 2 rangeland watersheds (average declivity 35 to 40%) following treatment with picloram, 2,4-D, and 2,4,5-T at 2.24 and 4.48 kg/ha in 1967 to 1970. Maximum amounts moved in surface water over an 8-mon period after application in August 1968 were 0.049 and 0.015% for 2,4-D and 2,4,5-T. LANE *et al.* (1977) also measured herbicide discharge at the watershed level in a similar rangeland environment. They applied 2,4-D, 2,4,5-T, picloram, and 3,6-dichloro-*o*-anisic acid (dicamba) in 4 different zones of increasing proximity to the stream channel to evaluate the contribution of runoff from different parts of the watershed to the total watershed runoff. If the data for all herbicides is combined, 0.21 to 0.56% of the applied herbicide was recovered in streamflow in 78 days after application. Discharge was greatest with the first runoff event of any size (Table XV). No 2,4-D was found in any samples of stream water, which is consistent with its application zone being furthest from the stream (80 to 90 m). The concentration of 2,4,5-T did not exceed 0.025 mg/L. The authors did not give data for discharge of specific herbicides, but inspection of their data on concentration makes it clear little 2,4,5-T was discharged. The relatively persistent and mobile dicamba and picloram which were applied closest to the stream were the major components of herbicide discharge.

Although limited in scope, these data (along with data on herbicide levels in stream water) suggest stream loading will be low from application of phenoxy herbicides on forest and rangelands. More data is needed in this area, but the findings available thus far are consistent with the short persistence-limited mobility characteristics of phenoxy herbicides in soil.

Table XIII. *Effects of environmental factors on the rates of loss of 2,4-D from water.*[a]

Process	Temperature	Oxygen concentration	pH	Light intensity	Formulation	Other factors	References
Ester hydrolysis	Minimized by lowered temperatures For Butoxyethyl ester[c] $\ln k_b \simeq \frac{-20.1}{Rt} + \frac{14.8}{R} + \ln \frac{kt}{h}$ $\ln k_a \simeq \frac{-17.6}{Rt} + \frac{21.3}{R} + \ln \frac{kt}{h}$ at 0°C $k_b \simeq 1\ sec^{-1} mole^{-1}$ $k_a \simeq 2.8 \times 10^{-6} sec^{-1} mole^{-1}$	No effect	$t½ = \frac{0.693}{k_a[H+] + k_b[OH-]}$ For the butoxyethyl ester hydrolysis rate is minimized at a pH around 4. At pHs $\gtrsim 5$ $t½ \simeq \frac{0.693}{k_b[OH-]}$ pHs $\lesssim 4$ relatively slow	n.r.[b]	See Section 2.1.1 and references in *National Research Council Canada* (1978) for details relating to particular ester formulations.	For more details see Section 2.1.1 in *National Research Council Canada* (1978). In sediments, the hydrolysis rates could be faster than those reported for aqueous solutions. Information is not available to illustrate this point. Since partitioning into the sediments will be minimized at pHs >4, this factor may be of little importance.	ZEPP *et al.* (1975)
Volatilization	Minimum as temperature decreases	No effect	Volatilization will be negligible for the acid and its salts at pHs > 4. pH should have little effect on the rates for the ester formulations prior to their hydrolysis	No effect	Significant losses could occur prior to mixing or in shallow ecosystems in the case of the more volatile ester formulations. For details see Section 2.2.1 of *National Research Council Canada* (1978) and references.		ZEPP *et al.* (1975) MACKAY & WOLKOFF (1973)
Microbial degradation	Pronounced effect not noted under aerobic or anaerobic conditions (slight reduction of rate in cold vs. warm aerobic conditions)	Aerobic conditions required for significant microbial degradation. Under anaerobic conditions, the half-life can exceed 80–120 days. Under aerobic conditions the half-life can be short, in the order of 1 to several wk.	n.r.[b]	n.r.[b]	n.r.[b]	Application of 2,4-D in previous seasons may increase rate. Conditions favoring partitioning into the sediments may increase rate under aerobic conditions—*i.e.*, formulation, pH, sediment, organic content must be considered.	DEMARCO *et al.* (1967) SCHWARTZ (1967) ALY & FAUST (1964)

Photolysis	Independent of temperature	Independent of oxygen concentration	n.r.[b]	Directly related to the intensity of radiation in the 280–320 nm range.	n.r.[b]	The significance of photolysis reactions is minimized during the winter months and in northern latitudes. Losses due to photolysis will be minimized in well-mixed deeper ecosystems.	Zepp *et al.* (1975)
Sorption	n.r.[b]	No effect	Only the ester and the molecular form of the acid are expected to partition to a significant extent into the sediments. pH will have little effect on esters prior to hydrolysis but pH < 3–4 required for other formulations.	n.r.[b]	See Section 2.2.2 of *National Research Council Canada* (1978) and pH.	The sediment partitioning should be related to the organic content of the sediments and, although not demonstrated, perhaps the nature of the organic material.	Pionke & Chesters (1973)

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[a] From Table 2.7, *National Research Council Canada* (1978).

[b] n.r. = not reported.

[c] k_a = acid hydrolysis, k_b = base hydrolysis, $\frac{k}{h} = \frac{\text{Boltzman constant}}{\text{Planck's constant}}$, and t = temperature in °K.

Table XIV. *Stream loading of phenoxy herbicides on 11 agricultural mini-watersheds in Ontario, 1975.*[a]

Watershed	Vol of water (x10 m^3)	Period	Herbicide	Loading (g)	Herbicide applied (%)	Months (%)
Big Creek	121	Mid Mar.–Dec.	2,4-D	66.5	0.014	May (0.2); June (89.1); July (3.9); Sept. (6.8)
			2,4,5-T	6.0	0.011	May (0.8); June (99.2)
Hillman Creek	65.5	Mid Mar.–mid Jan.	2,4-D	328	0.62	June (0.1); July (99.8); Nov. (0.1)
			MCPA	0.3		June (100)
Venison Creek	521	Feb.–Dec.	2,4-D	2.3	0.00037	July (100)
Canagagigue Creek	121	Mar.–Dec.	2,4-D	4.5	0.0026	June (43.1); July (0.1); Oct (0.4); Nov. (56.4)
			MCPA	2.7	0.0013	June (43.2); Oct. (0.4); Nov (56.4)
Little Ausable River	213	Early Apr.–early Jan.	2,4-D	2.8	0.00052	May (13.4); June (46.9); July (39.7)
Tributary of Maitland River	109	Late July–Dec.	2,4-D	3.0	0.00099	Oct. (100)
North Creek	79.5	Mid Apr.–mid Jan.	2,4-D	2.0	0.0035	June (100)
			2,4,5-T	2.0	—	June (100)
Tributary of Middle Thames River	88.9	Mid Apr.–mid Jan.	2,4-D	0.8	0.00041	June (49.4); July (50.6)
Shelter Valley Creek	460	Apr.–Dec.	2,4-D	4.4	0.0015	July (100)
			2,4,5-T	3.4		July (100)

[a] From Table 2.10, *National Research Council Canada* (1978); FRANK and RIPLEY (1977); FRANK *et al.* (1978).

Table XV. *Summary of runoff and herbicide yields from Watersheds 76.001 and 76.002 during the 1976 study.*[a]

Date of event	Days since treatment	Vol of runoff Event ($L \times 10^4$)	Vol of runoff Cumulative ($L \times 10^4$)	Yield of herbicides[b] Event (g)	Yield of herbicides[b] Cumulative (g)
		Watershed 76.001			
7/17/76	8	1.99	1.99	2.04	2.04
7/21/76	12	0.65	2.64	0.13	2.17
7/27/76	18	7.06	9.70	0.69	2.86
7/28/76	19	0.07	9.77	0.01	2.87
8/10/76	32	0.42	10.19	0.06	2.93
8/26/76	48	3.19	13.38	0.19	3.12
9/1/76	54	0.61	13.99	0.05	3.17
9/22/76	75	0.07	14.06	0.01	3.18
9/25/76	78	2.81	16.87	0.46	3.64
		Watershed 76.002			
7/17/76	8	0.69	0.69	0.95	0.95
7/21/76	12	0.03	0.72	0.05	1.00
7/27/76	18	7.36	8.08	8.41	9.41
8/26/76	48	5.49	13.57	0.53	9.94
9/25/76	78	2.40	15.97	0.64	10.58

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[a] From Table 4 of LANE *et al.* (1977).

[b] No 2,4-D from Zone 1 was found in any of the water quality samples.

e) Bioaccumulation of phenoxy herbicides

Bioaccumulation is the uptake (and at least temporary storage) by an exposed animal of a chemical from the environment. Generally, bioaccumulation is more likely to occur when organisms are exposed to persistent chemicals of low water solubility and high lipid solubility. The phenoxy herbicides do not meet any of these criteria to the degree of the chlorinated hydrocarbon insecticides. Organisms exposed to a phenoxy herbicide, however, will take up some of the chemical. Generally, the bioaccumulation ratios will be low and the residence time brief once exposure ceases.

The fate of phenoxy herbicides in terrestrial animals (usually laboratory or farm animals) has received considerable study. These studies show rapid excretion of these herbicides and little or no residue detectable in fat (or milk) more than a few days after exposure ceases (BJERKE *et al.* 1972, CLARK *et al.* 1975). Typically, more than 90% of phenoxy herbicide ingested is excreted unchanged in urine in 72 hr (PIPER *et al.* 1973 b, FANG *et al.* 1973, ERNE 1966).

NEWTON and NORRIS (1968) analyzed for 2,4-D and 2,4,5-T in a variety of tissues from blacktail deer collected in forest areas 15, 31, and 43 days after aerial application of herbicides. Measurable residues were found in at least one tissue from each animal collected. The highest concentrations occurred in stomach contents (0.36 mg/kg), feces (0.16 mg/kg), urine (0.19 mg/L), and in one animal, the thyroid (0.15 mg/kg). Concentrations in tissues normally consumed by human beings were <0.006 mg/kg in heart, and ranged from <0.006 to 0.017 mg/kg in kidney, <0.006 to 0.021 mg/kg in liver, and <0.006 to 0.010 mg/kg in muscle.

In a Minnesota forest, a wide variety of birds and animals (31 in total) was trapped 36 to 266 hours after application of 2,4-D. About 59% contained detectable residues of 2,4-D with the average residue of 1.97 mg/kg (range <0.1 to 25 mg/kg). Average residue levels declined with time after application (6.93 mg/kg at 1 day, 0.82 mg/kg at 2 days, and 0.36 mg/kg at 14 days after application) (*U.S. Department of Agriculture, Forest Service* 1977).

As part of a widespread survey of the Swedish environment for phenoxy herbicide residues, ERNE (1974 and 1975) reported only 3% of 330 samples of muscle from healthy fish (several species from 120 locations) contained detectable residues of 2,4-D or MCPA. Residues ranged from 0.05 mg/kg to 1.5 mg/kg. Of 250 samples from wildlife found dead (numerous species including grouse, hare, deer, moose, and others), 25% of the samples of liver and kidney contained detectable residues, mostly 2,4-D and/or 2,4,5-T. The residue levels in liver and kidney were fairly low, the maximum value was 6 mg/kg in a roe deer kidney. Most of the values were <1 mg/kg. In 130 samples of liver and kidney from healthy moose, roe deer, and hare (shot in herbicide-treated forest areas), phenoxy residues were found in 42 animals (32%). Residues were all <4.5 mg/kg and most were <1 mg/kg. There was no marked difference in the pattern of residues between the group of animals found dead and those that were shot. However, only 2 of 60 (3%) of animals shot in untreated forest areas contained detectable residues.

GARCIA and RHODES (1979) reported residues of 2,4,5-T in muscle tissue of about 50% of the coots (*Fulica americana*) they collected around a lake which received runoff from Texas rangeland areas sprayed with 2,4,5-T. The average residue level detected was 0.2 mg/kg. A few birds had residues which averaged 0.02 mg/kg in fat, 0.04 mg/kg in liver, and 0.02 mg/kg in the gizzard.

In the aquatic environment, more work has been done on bioaccumulation, and generally uptake is limited and residence time brief. In an area treated with 1.12 kg/ha of 2,4-D ester (granular), mussels contained 0.38 and 0.70 mg/kg reflecting their consumption of algae which had absorbed the herbicide. Fish, on the other hand, did not contain detectable residues (<0.14 mg/kg) (SMITH and ISOM 1967). SCHULTZ and WHITNEY (1974) report 2,4-D residues in a variety of fish species ranged from undetectable to 0.162 mg/kg; about 80% did not contain detectable residues after application of 4.48 kg/ha of 2,4-D amine salt ae. SIGMON (1979) reported no measurable (<0.05 mg/kg) residues of 2,4-D in bluegill sunfish after 8 days in water containing 3 mg/L of 2,4-D as the butoxyethanol ester. 2,4,5-T residues ranged from 0.06 to 0.12 mg/kg under similar conditions.

Yockim *et al.* (1978) did an extensive bioaccumulation study with 2,4,5-T in a model aquatic ecosystem where the initial concentrations of 2,4,5-T in sediment were 0.1, 1.0, and 10 mg/kg (corresponding levels in water were 1.8, 15.2, and 143.2 mg/L 32 days later). Bioaccumulation ratios were highest in algae (about 50) and lowest in snails (about 5). Residue levels declined rapidly when the organisms were placed in fresh water for 7 to 14 days (Table XVI). Virtanen *et al.* (1979) studied the fate of MCPA and 4,6-dichloro-*o*-cresol (a 0.5%-level impurity of MCPA) in a model terrestrial ecosystem (Table XVII). They found rapid reduction of MCPA levels in terrestrial vegetation and some movement of MCPA to the water but no uptake of MCPA by aquatic plants. Both fish and snails contained detectable residue of MCPA but at levels less than the level in water, indicating no (or only a low) tendency for bioaccumulation. No residues of 4,6-dichloro-*o*-cresol were detected in any part of the system which authors attribute to its rapid degradation to the corresponding catechol.

IV. The behavior of TCDD in the forest

Much of the controversy about the use of 2,4,5-T and silvex in forestry involves 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). TCDD is produced as a by-product during one of the manufacturing steps of these herbicides. Although it is present in only minute quantities [EPA guidelines are <0.1 mg/kg; current production grade 2,4,5-T contains <0.03 mg/kg, according to Thomas (1980)], it is highly toxic.

The chemical, physical, and biological properties of TCDD and its toxicology and behavior in the environment have been intensely investigated since 1970. An excellent summary of research on TCDD through 1972 is in the proceedings of an international conference held in April 1973 (*U.S. Department of Health, Education and Welfare* 1973). More recent reviews are provided by the *National Research Council of Canada* (1978), Turner (1977), *Swedish National Research Council* (1978), and Blair (1973).

The extremely small quantities of TCDD which are likely to be present in environmental samples have forced the development of the most rigorous and sensitive analytical methodologies yet developed for chemicals in the environment (Baughman and Meselson 1973, Hummel 1977, Shadoff and Hummel 1978, O'Keefe *et al.* 1978). These methods are now yielding data that will be of substantial value in establishing the environmental behavior of TCDD in the field and the degree to which theoretical and laboratory studies accurately predict this behavior.

a) Photochemical degradation

Crosby *et al.* (1971) reported pure crystalline TCDD was not subject to photolysis, but Plimmer *et al.* (1973) showed a hydrogen donor was

Table XVI. *Tissue concentrations and bioaccumulation ratios of ^{14}C-2,4,5-T and ^{14}C-TCDD in aquatic organisms as a function of time.*[a]

Organism and chemical	Initial[b] soil conc.	Time (days)						
		Adsorption[c]					Desorption[d]	
		1	3	7	15	32	39	46
Water fleas								
2,4,5-T	0.1	2.2[e](4)[f]	4.0 (4)	1.2	21.5	27.4 (15)	—	—
	1.0	4.5 (1)	15.4 (2)	171.4	127.0	243.6 (16)	—	—
	10.0	36.9 (1)	—	3,423.9	—	1,368.7 (10)	—	—
TCDD	0.1	6.8 (2,000)	12.2 (4,207)	17.1 (7,125)	8.6 (3,308)	7.4 (1,762)	—	—
Fish[g]								
2,4,5-T —1	0.1	2.0 (3)	10.4 (12)	9.6	17.5	42.2 (23)	15.1	—
	1.0	12.3 (2)	33.1 (4)	30.0	82.5	224.8 (15)	167.2	—
	10.0	1,262.0 (19)	1,032.0 (10)	347.4	680.8	3,729.3 (26)	3,104.9	—
TCDD —1	0.1	2.3 (676)	4.8 (1,482)	11.7 (4,875)	*[h]			
TCDD —2		0.9	2.3	4.1	5.9	*[i]		
Algae								
2,4,5-T	0.1	3.1 (5)	3.2 (4)	10.2	52.0	87.6 (49)	57.4	29.5
	1.0	41.2 (7)	16.4 (2)	120.7	359.0	732.2 (48)	538.9	291.8
	10.0	105.5 (2)	106.4 (1)	1,072.3	5,525.1	6,125.8 (43)	5,581.1	3,769.2
TCDD	0.1	0.02 (6)	3.0 (1,034)	5.0 (2,083)	1.7 (654)	4.2 (1,000)	2.1	1.0
Snail								
2,4,5-T	0.1	1.7 (3)	3.2 (4)	2.6	10.4	10.6 (6)	8.0	5.4
	1.0	8.3 (1)	8.4 (1)	9.6	54.3	50.6 (3)	39.7	97.4
	10.0	39.8 (1)	34.0 (0)	122.5	1,641.5	585.0 (4)	805.4	836.5
TCDD	0.1	2.5 (735)	3.6 (1,241)	5.0 (2,083)	9.7 (3,731)	5.8 (1,381)	0.5	1.6

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[a] From Table 2 of Yockim *et al.* (1978).

[b] 2,4,5-T in ppb (μg/kg), TCDD in ppt (ng/kg).

[c] Adsorption = period when organism was in ecosystem with test chemical.

[d] Desorption = period when organism was removed to untreated water.

[e] Tissue level in ppb.

[f] Bioaccumulation ratios = tissue concentration/water concentration.

[g] Fish 1 = *Gambusia affinis* and 2 = *Ictalurus punctatus*.

[h] All fish died by day 15 with tissue levels of 7.2 ppb.

[i] Fish had died by this date with tissue levels of 4.4 ppb.

Table XVII. *MCPA in a model aquatic-terrestrial ecosystem treated with MCPA at 5 kg/ha. Each value represents the mean of 2 experiments with 2 model replicates.*[a]

	Residues of MCPA (mg/kg)			
	Days after application			
Substrate	3	6	12	CF[b]
Terrestrial plants	27.7	11.98	3.15	
Soil	0.196	0.096	0.114	—
Water	0.045	0.121	0.156	—
Water plants	0	0	0	0
Fish[c]	0.024	0.005	0.020	<1
Snail	0.866	0.577	0.075	<1
Mouse[d]				
Liver	0	0	0.52	3.25
Kidney	0	0	0.64	4.00

[a] From Table 2 of Virtanen *et al.* (1979).

[b] $\text{CF} = \dfrac{\text{concentration in the organism}}{\text{concentration in water}}$

[c] MCPA was found in only 1 fish.

[d] MCPA was found in liver and kidney of 1 mouse.

necessary, and TCDD decomposed rapidly when dissolved in methanol and exposed to UV light. Dobbs and Grant (1979) studied the photolysis of a series of chlorinated dibenzo-*p*-dioxins by sunlight and found they degrade to less toxic forms in sunlight. Gebefuegi *et al.* (1977) studied TCDD photochemical degradation under simulated environmental conditions. They reported degradation rates of 92% in longwave UV and 98% in short UV in 7 days. Their findings suggest the possibility of the photodegradation of TCDD in sufficient sunlight even in the absence of organic proton donors.

b) Vegetation—residues and fate

Crosby and Wong (1977) analyzed the persistence of TCDD in herbicide formulations on leaves, soil, or glass plates (Fig. 4). When exposed to natural sunlight (full summer sun), most of the TCDD on leaves disappeared in less than 6 hr. This loss was due principally to "photochemical dechlorination." The herbicide formulation provided a hydrogen donor which allowed rapid photolysis to occur. Norris (1980) reported rapid disappearance of TCDD from leaves even under the low light condition of a cloudy day. A half-life of 7 to 10 hr was observed when the UV energy (295 to 385 nm) input was 28 to 43 KJ/m²/hr. In contrast, full summer sunlight delivered about 150 KJ/m²/hr at this study site. The author noted, however, that volatilization as well as photodecomposition may be responsible for the disappearance noted.

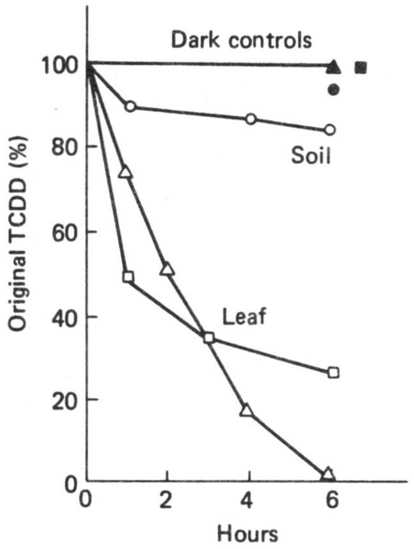

Fig. 4. Disappearance of TCDD from leaves, soil, and glass in sunlight (CROSBY and WONG 1977).

Laboratory studies indicate uptake of TCDD from soils by plants may not be significant. Soybean and oat plants took up only trace amounts of TCDD in the first 10 to 14 days after exposure to sandy soil containing 200,000 times the amount of TCDD contained in an application rate of 2.24 kg/ha of 2,4,5-T (with 0.1 mg/kg of TCDD). No detectable TCDD was in the grain or beans at maturity. COCUCCI *et al.* (1979), however, reported TCDD in leaves, twigs, fruit, and cork of several woody plants growing in soil that had been contaminated by the release of TCDD at Seveso, Italy. The twigs and cork material were present at the time of the TCDD release, but the fruit and leaves were not. The residues found in a cherry tree were: leaves—1.01 μg/kg, fruit—0.395 μg/kg, twigs—13.14 μg/kg, and cork—3.16 μg/kg. These results indicate TCDD is mobile in plants, at least to a small degree. The underground and aerial organs of carrot, potato, onion, and narcissus contained detectable levels of TCDD, but the concentration was usually less than the concentration in soil. The TCDD level in underground organs decreased markedly (10- to 30-fold decrease) in 2 to 4 mon when the plants were transplanted to unpolluted soil (Table XVIII). TCDD was not translocated from the point of application on the leaf surface to other parts of the plant, and some was washed off with rain water (ISENSEE and JONES 1971). In another field study by CHENEY *et al.* [no date], no TCDD was detected in samples of foliage collected 1, 2, 4, and 8 days after application of 3.36 kg/ha of 2,4,5-T PGBE ester. SUNDSTROM *et al.* (1979) reported only 1 of 8 samples of vegetation from 6 reforestation areas sprayed with 2,4,5-T

Table XVIII. *TCDD in soil and vegetation, Seveso, Italy.*[a]

		Residue in underground parts (μg/kg)				
Soil[b] (μg/kg)	Vegetation	Aerial parts	Inner	Outer	When transplanted to unpolluted soil	After time in unpolluted soil
5.310	Carrot	2.150	9.203	4.462	8.90	0.760[c]
8.330	Potato	2.115	1.961	3.560	1.86	No value[e]
2.680	Onion	0.835	1.763	1.798	2.26	0.062[d]
4.370	Narcissus	1.658	2.593	2.221	2.62	0.022[e]

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[a] From Tables 1 and 2 of Cocucci *et al.* (1979).

[b] 10-cm diameter soil cores, 14 cm long.

[c] Transplanted without aerial parts, harvested 4 mon later.

[d] Transplanted with aerial parts, harvested 4 mon later.

[e] Transplanted without aerial parts, harvested 10 mon later.

(*n*-butyl, isobutyl ester mixture, or 2-butoxyethyl ester) contained detectable TCDD (170 ng/kg TCDD). The ratio of TCDD to 2,4,5-T was lower in the vegetation than in the formulation, which suggests more rapid disappearance of TCDD than of 2,4,5-T.

c) Soil—residues and fate

KEARNEY *et al.* (1972) indicated that pure TCDD on soil surfaces was not degraded by sunlight. CROSBY and WONG (1977) demonstrated that TCDD in formulated herbicide is rapidly degraded (about 15% in 6 hr) on the soil surface by the action of sunlight (Fig. 4). TCDD was immobile in 5 soils with widely varying properties (HELLING *et al.* 1973). The possibility of TCDD entering groundwater is remote (TSCHIRLEY 1971). If TCDD is incorporated into soil, it disappears slowly. About half the TCDD was lost after 1 yr in a laboratory study (KEARNEY *et al.* 1972). It seems unlikely, however, that TCDD would be incorporated in soils under most conditions of use, since it does not leach into the soil. TCDD is not produced from breakdown products of 2,4,5-T in soils or in sunlight (KEARNEY *et al.* 1973 a and b).

d) Water—residues and fate

TCDD is nearly insoluble in water, about 0.0002 mg/L. For this reason, it would be expected to remain on plant and soil surfaces at the application site. Because it is immobile in soils, KEARNEY *et al.* (1973 b) concluded there would be "no ground water contamination problem." These properties suggest TCDD is unlikely to enter forest streams via leaching or overland flow. Direct application or drift of 2,4,5-T or silvex to water will also result in entry of TCDD to the water. TCDD would most likely be associated with the less water-soluble constituents of formulation which may form a thin film on water surfaces (MACKAY and WOLKOFF 1973). TCDD in such films should be rapidly degraded by sunlight, much like the thin films on vegetation and soil studied by CROSBY and WONG (1977).

WARD and MATSUMURA (1978), studying the fate of TCDD in a model aquatic ecosystem, reported a strong partition (about 95%) in favor of TCDD adsorption to sediments. TCDD half-life in the sediment (incubated in the laboratory anaerobic conditions, underwater) was about 600 days. The concentrations used in the experiment were high (0.7 to 1.8 mg/kg TCDD), more than 10^6 times greater than would be expected from normal rates of application of 2,4,5-T. The effect of concentration on rate of loss is not known. YOCKIM *et al.* (1978) also used very high levels of TCDD in sediment (0.1 mg/kg) in a model aquatic ecosystem study. They found the TCDD equilibrated between sediment and water phases in about 1 day with about 3 ng/L of TCDD in water and 0.1 mg/kg of TCDD in sediment (a 33,000:1 distribution ratio between sediment and water). They noted an 18% decrease in TCDD level in the sediment between 30 and 150 days of incubation (if the decrease was linear with time, the half-life was 333 days in this system).

The actual levels of TCDD in vegetation, forest floor, soil, and water from the field have been measured in only a few cases. They can be estimated, however, from initial residue levels of 2,4,5-T (Norris *et al.* 1977) (assuming 2,4,5-T contains 0.1 ppm TCDD), and assuming the TCDD persistence characteristics reported by Crosby and Wong (1977), Kearney *et al.* (1973 a and b), and Miller *et al.* (1973) apply (Table XIX). Verification of these values is needed from actual residue studies.

e) Bioaccumulation

TCDD is present in such minute quantities in the environment that primary exposure to TCDD (that is, exposure resulting from direct ingestion, dermal absorption, or inhalation) is limited (Norris *et al.* 1977). Bioaccumulation is a mechanism by which organisms may collect or concentrate TCDD from primary exposure. If significant bioaccumulation occurs, these organisms (as food sources for other creatures) could possibly carry toxicologically significant residues. The question is, then, does bioaccumulation of TCDD occur and, if it does, to what degree does it occur in connection with normal patterns of use of 2,4,5-T and silvex? There are three ways to study this question: physical-chemical properties, laboratory studies, and environmental monitoring.

1. Physical-chemical properties.—Physical-chemical properties are good indicators of the potential for bioaccumulation. Chemicals with low water solubility and high fat solubility have a strong potential for bioaccumulation. DDT is an example of a chemical which is low in water solubility (0.001 mg/L), high in fat solubility (86,000 mg/L in corn oil),

Table XIX. *Calculated residues of TCDD in the forest after aerial application of 2,4,5-T (containing 0.1 mg/kg TCDD) at 2.24 kg/ha.*[a]

Time after application (days)	Vegetation (ng/kg[b])	Forest floor (ng/m²)	Soil (ng/kg[b])	Water (ng/L[b])
0	5	4	0.001	1
1	0.001[c]	0.5[c]	0.001[d]	1×10^{-6}[e]
4	—	0.004	0.0009	—
16	—	—	0.0008	—
26	—	—	0.0006	—
52	—	—	0.0005	—

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[a] Calculated from Norris *et al.* (1977).

[b] Part per trillion.

[c] Assumes TCDD persistence reported by Crosby and Wong (1977).

[d] Assumes TCDD persistence reported by Kearney *et al.* (1973 a and b).

[e] Assumes TCDD persistence reported by Miller *et al.* (1973).

and is known to bioaccumulate in exposed organisms. TCDD is low in water solubility (0.0002 mg/L) but is also low in fat solubility (47 mg/L in corn oil). The ratio of oil solubility to water solubility is 86×10^6 for DDT and 0.2×10^6 for TCDD. These physical-chemical properties suggest that TCDD would bioaccumulate in exposed organisms but probably to a lesser degree than DDT. The degree of bioaccumulation is likely to depend on the magnitude and duration of organism exposure.

2. Laboratory studies.—Bioaccumulation can also be studied in animal feeding studies or in small laboratory ecosystems. In laboratory feeding studies involving repeated exposure to TCDD, FRIES and MARROW (1975) reported that after 6 wk of exposure, the TCDD level in rats reached a steady-state which was 10.5 times the daily intake. ROSE *et al.* (1976) also reported steady-state concentration in rats in 7 wk (slightly more then 10 times the daily intake level). In a feeding study with rainbow trout, HAWKES and NORRIS (1977) reported limited data indicating that on a whole-body basis, TCDD levels in fish were approximately of the same order of magnitude as the level of TCDD in the food which they consumed. These data indicate that animals which ingest TCDD in their diet will accumulate TCDD to body burdens about 10 times the concentration in the diet and that certain body tissues will contain residues for at least as long as exposure continues.

TCDD was not irreversibly accumulated in these feeding studies, and once exposure to TCDD stopped, the body burden decreased. PIPER *et al.* (1973 a), ALLEN *et al.* (1975), FRIES and MARROW (1975), and ROSE *et al.* (1976) all found a half-life for TCDD residence in the body which ranged from 12 to 30 days.

Several laboratory-scale aquatic ecosystem studies have been conducted with TCDD. MATSUMURA and BENEZET (1973) exposed several aquatic organisms to TCDD in such a system; unfortunately, in most instances the concentration of TCDD in the water was substantially in excess of the limits of its solubility which prevents meaningful interpretation of the data. In one experiment, however, TCDD was adsorbed on sand in the bottom of the aquariums and they found 0.0001 mg/L of TCDD in water and 0.157 mg/kg in brine shrimp, to give a concentration factor or bioaccumulation ratio of 1,570:1. The bioaccumulation ratio is the ratio of the concentration of TCDD in the organism to the concentration of TCDD in the water.

ISENSEE and JONES (1975) also used a laboratory-scale, aquatic ecosystem to study TCDD bioaccumulation in mosquito fish, fingerling channel catfish, algae, duckweed, snails, and water fleas. TCDD was adsorbed on soil which, when equilibrated with the water, resulted in TCDD concentrations in water ranging from 0.05 to 1,330 ng/L. Concentrations in excess of 200 ng/L exceed the limits of water solubility for TCDD and prevent meaningful interpretation of those bioaccumulation data. In experiments where the water concentration was less than 200 ng/L, Isensee and Jones (1975) reported bioaccumulation ratios ranging from 2×10^3 to 63×10^3. They found a strong positive correlation between the concentration of TCDD in tissue and concentration of TCDD in water for all organisms. The total amount of TCDD accumulated was proportional to its concentration in water, and equilibrium concentrations in tissues were reached in 7 to 15 days. They reported TCDD bioaccumulated to about the same magnitude as many of the organochlorine insecticides in model aquatic ecosystems.

Yockim *et al.* (1978) used basically the same technique as Isensee and Jones (1975). They reported generally increased TCDD accumulation with time in water fleas, fish, algae, and snails, but the levels appeared to decline when the organisms were placed in clean water for periods of 7 to 14 days (Table XVI). The bioaccumulation ratios during the period of exposure ranged from 2×10^3 to 7×10^3 with the highest ratios in water fleas and the lowest in algae. Miller *et al.* (1979) exposed young coho salmon to TCDD in water for periods ranging from 1.5 to 96 hr and then transferred the fish to clean water. After 114 days in clean water, whole-body residues contained from 4 to 48% of the TCDD originally placed in the exposure container. The residue levels increased linearly with duration of exposure. The reason TCDD clears more slowly from aquatic organisms than terrestrial animals once exposure ceases is not known. The apparent persistence of the whole-body residues of TCDD in fish indicates analysis of fish may provide a sensitive technique for detecting the presence of TCDD in aquatic ecosystems in the field.

These results from laboratory studies indicate that organisms exposed to TCDD in their diet or in aquatic ecosystems will bioaccumulate TCDD. The degree of bioaccumulation which occurs from the use of TCDD-contaminated herbicides in natural ecosystems depends on the magnitude and duration of organism exposure. In laboratory studies, organism exposure is assured through regular addition of TCDD to the food or (in aquatic ecosystems) from a substantial reservoir of TCDD adsorbed on sand or soil which continuously releases small quantities of TCDD to water.

In the natural environment, several processes operate to reduce or eliminate TCDD exposure to organisms and thereby minimize the opportunities for bioaccumulation. Crosby and Wong (1977) reported TCDD in herbicide formulations disappeared rapidly from vegetation and soil when exposed to sunlight. This mechanism would markedly reduce or eliminate organism exposure through dermal contact with or ingestion of contaminated vegetation. In the aquatic environment, the likelihood of 2,4,5-T and TCDD entry to aquatic systems is slight; but if it does occur, chemicals in the water are rapidly diluted and carried downstream with streamflow. TCDD which adsorbs on sediments provides a reservoir of TCDD in the aquatic environment similar to that provided in the model aquatic ecosystem studies. In real stream systems, TCDD desorbed from sediments would be quickly moved downstream with streamflow, thus the opportunity for bioaccumulation by a particular organism would be limited.

3. Environmental monitoring.—The third approach to evaluating TCDD bioaccumulation is to look directly for evidence of bioaccumulation in the field. Several efforts have been made but with markedly different levels of sophistication and sensitivity of analytical methods. For instance, WOOLSON *et al.* (1973) analyzed samples of eagle tissues from various regions in the United States. No TCDD was detected, but the minimum detection limit of 50 μg/kg is not adequate to properly evaluate bioaccumulation of TCDD. Similarly, GARCIA and RHODES (1979) did not detect TCDD in American coots collected near a lake which received runoff from rangeland areas sprayed with 2,4,5-T. They did not specify their minimum level of TCDD detection, but it appeared to be about 1 μg/kg.

YOUNG *et al.* (1976 and 1978) studied the behavior and bioaccumulation of TCDD in animals from the Eglin Air Force Base site used for equipment development and testing for application of herbicides in Vietnam. The study area received massive applications (500 to 1,000 kg/ha) of 2,4,5-T, much of which contained TCDD in excess of 1 mg/kg. Analysis of soil from the test site showed TCDD residue levels in the range of 10 to 1,500 ng/kg several yr after residue applications had stopped. Analysis of rodents, reptiles, birds, fish, and insects shows the presence of TCDD in tissues of at least some of the organisms from this area. The level of TCDD in the herbicide used at the Elgin test site and the massive rates of application make these data not directly applicable to the registered uses of 2,4,5-T and silvex in the United States.

Studies done in connection with the registered uses of 2,4,5-T for vegetation control have found relatively little TCDD in biological samples. In 1973–74, the Environmental Protection Agency, cooperatively with the USDA Forest Service, conducted a monitoring program for TCDD in tissues of animals from several areas which had been recently treated with 2,4,5-T in western Oregon and Washington. The analytical methodology employed, however, was not adequate to establish the presence of TCDD in those environmental samples. It was adequate to determine which samples did not contain TCDD in the low-to-mid part-per-trillion range. Approximately 84% of the samples did not contain detectable levels of TCDD. The remaining samples were described by EPA as "minutely suggestive" for TCDD. In 1976, 5 of these "possible positive" samples were reanalyzed by 2 laboratories (participants in the dioxin monitoring program); 2 samples did not contain detectable TCDD. EPA described the results of analysis of the other 3 as follows: "Some of the samples analyzed in 1973–74 still appear positive for TCDD. Unfortunately, the results from the two laboratories participating in the confirmation vary widely. The confirmation analysis, therefore, still does not give a precise quantification of the amount of TCDD present. It does appear, however, that from a qualitative standpoint TCDD was present in a small percentage of the forest samples collected in 1973." Assuming 3 out of 5 samples (60%) which were possible positives in the 1973–74 analysis are, in fact, qualitative for TCDD, then 9.6% of the 1973 samples were positive for TCDD and 90.4% did not contain detectable residues (*U.S. Department of Agriculture, Forest Service* 1978 c).

Norris (1980) reported first results from a survey of 6 Oregon forest stream systems for TCDD. More than 80 samples of fish from 23 sampling stations were analyzed to a detection limit of less than 10 ng/kg. All the fish were negative for TCDD at 10 ng/kg, but 5 (one a control) were reported as possible positives at 0.2 to 0.4 ng/kg greater than the limits of detection. Of the 6 stream systems surveyed, 4 have an extensive history of 2,4,5-T application.

The U.S. Environmental Protection Agency (EPA) beef-fat-monitoring program which was initiated in 1974 has been completed. Samples of beef fat (85) and liver (43) have been analyzed for TCDD. Approximately 25% of these samples are from animals not exposed to areas sprayed with 2,4,5-T. The *U.S. Environmental Protection Agency* (1977 a) reported that 1 sample showed a positive TCDD level at 60 ng/kg and 2 at 20 ng/kg; 5 samples appeared to have TCDD in the range of 5 to 10 ng/kg. EPA stated, "The analytical method is not valid below 10 ppt, although a recent dioxin implementation plan meeting statement set 9 ppt as the minimum detectable level." Of the 43 liver samples analyzed, 1 sample might contain TCDD, but the level is too close to the sample detection limits for quantification. A fat sample from the same animal showed no TCDD residue. The results of the EPA beef-fat-monitoring study indicate bioaccumulation of TCDD in grazing animals is not sufficient to result in regularly detectable levels of TCDD (>10 ng/kg) in beef fat and liver.

Newton and Snyder (1978) reported on the analysis of livers from mountain beavers (*Aplodontia rufa*) captured 2 mon after a forested area in western Oregon was treated with 2,4-D and 2,4,5-T. Mountain beavers have a small range and are herbivorous, thereby affording them substantial exposure to herbicide-treated plants. In addition, they are a burrowing animal which will put them in intimate contact with herbicide and TCDD present on the soil surface. Analysis showed no detectable levels (<10 ng/kg) of TCDD. Shadoff *et al.* (1977) looked for TCDD accumulation in animals due to the use of 2,4,5-T and silvex in the midwestern United States. They did not detect any TCDD (detection limit about 10 ng/kg) in samples of fish, water, mud, and human milk from areas in Arkansas and Texas.

Meselson and O'Keefe (1977), in a preliminary report to Oregon Congressman Weaver, indicated some samples of human milk from residents of areas in which 2,4,5-T was used contained detectable levels of TCDD (3 samples out of 6 from Texas, and 1 sample out of 5 from

Oregon). The levels detected were at the limits of detection and were substantially below the 10 ng/kg level established by EPA in the beef-fat-monitoring program as the minimum acceptable, reportable level. Recently, the *U.S. Environmental Protection Agency* (1980) announced results of analysis of samples of milk from 105 human beings selected from areas in California, Oregon, and Washington where the dioxin-containing herbicides were known to have been used for several yr. No residues of TCDD were detected at levels of detection that varied from 1 to 4 ng/kg.

4. Conclusions about bioaccumulation.—The results of these various tests indicate that if TCDD is present in the environment in a form which is available to organisms, then bioaccumulation will occur if organisms are exposed. The degree to which bioaccumulation of TCDD occurs in the field is dependent not only on the physical-chemical properties of the compound but also on the persistence and availability of TCDD in the environment.

Monitoring efforts indicate that substantial bioaccumulation of TCDD (sufficient to produce residue levels in excess of 10 ng/kg of TCDD in the majority of the population) is not occurring in animals in or near areas treated with 2,4,5-T or silvex in operational programs. Apparently mechanisms of degradation and dilution which operate in the natural environment reduce the opportunities for organisms to be exposed, and thereby reduce the degree to which TCDD bioaccumulation occurs.

This conclusion is not in conflict with recently reported findings of TCDD in fish from the Titawabasee River downstream from the Dow Chemical Co. manufacturing plant at Midland, Michigan (*Dow Chemical Co.* 1978 a). The residues in the fish, whether they are from plant discharge water or are from the products of combustion (*Dow Chemical Co.* 1978 b), did not result from the use of 2,4,5-T as an herbicide.

f) Thermal conversion of 2,4,5-T to TCDD

It is possible to produce TCDD on heating or burning of 2,4,5-T or 2,4,5-T-treated materials in laboratory tests. The conditions of combustion and herbicide concentration are crucial. The tests reported by BUU-HOI *et al.* (1971), LANGER *et al.* (1973 a), and others showed TCDD formation occurred when 2,4,5-T was heated in a closed container under alkaline conditions such that the sodium salt of trichlorophenol was a significant degradation product. The amount of herbicide employed in these tests was very high. LANGER *et al.* (1973 b) indicated control of the decomposition reaction to produce trichlorophenol was necessary since heating above the decomposition point (300°C) produced no TCDD. AHLING *et al.* (1977) studied both the destruction of 2,4,5-T and the formation of polychlorinated dibenzo-*p*-dioxins. They noted 99.995% decomposition of the 2-butoxyethyl ester of 2,4,5-T maintained at 400° to 500°C for 2 sec. However, about 3 mg of one or more 4-chlorodibenzodioxin isomers were formed for each kg of formulation burned. The emission decreased with increased temperature and time. At 850°C and at times greater than 0.9 sec, none, or barely detectable levels of 4-chlorodibenzodioxin were formed.

Concentration of herbicide is important because the formation of TCDD from chlorophenols is apparently a bimolecular reaction. If conditions of heat and alkalinity are conducive to the condensation of the phenol to form TCDD, then the extent of condensation varies with the number of molecules available to interact with one another. In the experiments reported by AHLING *et al.* (1977), the concentration of 2,4,5-T (10,000 mg/kg of wood chips) was about 50 to 500 times higher than levels reported in leaves.

Experiments such as those of LANGER, AHLING, and others are useful because they show that thermal production of TCDD is chemically possible. They drastically overestimate, however, the levels of TCDD which might be produced by burning in the field because in the laboratory tests (1) the concentrations of herbicide were several times greater than the levels of 2,4,5-T which occur in the field and (2) heating was prolonged, uniform, and combustion did not always occur. Temperatures at which thermal decomposition of TCDD occurs (800°C) were not usually attained in these tests. Actual burning, of course, will produce temperatures as low as those used in laboratory tests only briefly. As burning temperatures approach 800°C, thermal decomposition of TCDD occurs (AHLING *et al.* 1977). When combustion can take place with a free exchange of air, temperatures above 1,200°C are common. Under these conditions, complete oxidation of 2,4,5-T, trichlorphenols, TCDD, and similar chemicals is expected to occur.

There are only limited experimental data on how much TCDD is produced when 2,4,5-T is burned. WATTS and STORHERR (1973) noted burning and heating of such 2,4,5-T-treated products as vegetation, meat, and fat did not produce detectable TCDD. The sensitivity of their analysis, however, was not adequate to detect environmentally important quantities of TCDD. The most pertinent data came from a laboratory experiment in which grass treated with 2,4,5-T at 12 lb/A was burned under conditions somewhat resembling those which might occur in the field (STEHL and LAMPARSKI 1977). Their study showed an approximate 0.00016% conversion of 2,4,5-T to TCDD. This involved a semiclosed system, however. Thus, any TCDD which might normally have been lost to the air as vapor or adsorbed on smoke particles in forest burning was captured and retained in this system.

The amount of TCDD likely to be produced on burning treated vegetation is dependent on the concentration of 2,4,5-T in the vegetation. NORRIS *et al.* (1977) determined the persistence of 2,4,5-T in Oregon forests. Calculated levels of TCDD which might be produced by burning vegetation containing 2,4,5-T according to NORRIS *et al.* (1977) and assuming the conversion ratio reported by STEHL and LAMPARSKI (1977)

Table XX. *2,4,5-T residues on vegetation (measured) and TCDD (calculated) that might be produced by burning vegetation.*

Mon after application	2,4,5-T[a] (mg/kg)	Possible TCDD level if burning occurs at time indicated[b] (ng/kg)
0	95	152
1	9.1	14
3	0.10	0.16
6	0.07	0.11
12	0.01	0.02

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[a] From NORRIS *et al.* (1977).

[b] Assumes conversion is 0.00016% (STEHL and LAMPARSKI 1977).

are in Table XX. AHLING *et al.* (1977) calculated the formation of 4 chlorodioxins (presumably including TCDD) could be as high as 1 $\mu g/m^2$ in a forest fire directly after application of herbicide. They believe, however, the amount is likely to be smaller because the concentration of 2,4,5-T would normally be less. The data of NORRIS *et al.* (1977) and STEHL and LAMPARSKI (1977) indicate levels of 0.02 $\mu g/m^2$ if burning occurs immediately after application and <0.002 $\mu g/m^2$ if burning occurs 1 mon later.

RAPPE (1978) (reporting the unpublished research of Anderson *et al.*) noted that burning "sprayed and spiked" vegetation at 600°C did not produce TCDD (<4 mg TCDD/kg of 2,4,5-T) in combustion gases, soot particles, and ash. The degree of conversion was <1 mg of TCDD/kg 2,4,5-T at 550° to 950°C in another study (unpublished research of AHLING *et al.*) according to RAPPE (1978).

Clearly, the amount of TCDD produced by combustion of sprayed vegetation depends to a major degree on when burning occurs after treatment. 2,4,5-T is occasionally used to desiccate brushfields prior to burning. Burning which takes place from 1 to 3 mon after the application could result in TCDD levels of 14 and 0.2 ng/kg, respectively. In some brush types, burning is delayed for 12 mon or more. Immediately after application the level of TCDD present on the vegetation may be about 10 ng/kg, assuming the 2,4,5-T contained 0.1 mg/kg TCDD. Data of CROSBY and WONG (1977) indicate the TCDD originally applied will be mostly gone within 1 mon of the application. Therefore, the levels of TCDD which might be produced are not expected to substantially exceed TCDD levels present as a result of the original application of herbicide.

Preliminary results from the *Dow Chemical Co.* (1978 a and b) indicated several dioxin isomers may be formed in trace amounts during the combustion of many substances (not contaminated with or associated with

2,4,5-T). Fossil fuels, automotive exhaust, trash burners, cigarette smoke, and charcoal-grilled meats have all been found to produce or contain minute quantities of various dioxin isomers, including in some cases the 2,3,7,8-tetrachloro isomer. These sources of dioxins are not associated with the registered uses of 2,4,5-T as an herbicide in any way.

Summary and conclusions

The phenoxy herbicides have the most extensive scope and longest history of use of any group of pesticides in forestry. There is extensive literature on the behavior of the phenoxy herbicides, but their use in forestry remains controversial. Risk assessment is the predominant issue.

Despite the large number of citations in this review, not all aspects of this topic have been fully cited. The greatest strengths in the literature involve 2,4,5-T movement and persistence in the major forested regions of the United States. Both the magnitude and duration of exposure that organisms are likely to receive (via vegetation, forest floor, soil, or water) can be estimated with the available data. Despite the fact 2,4-D is used far more extensively than 2,4,5-T, it has received substantially less research attention. Public and regulatory pressure to ban this chemical is increasing and, as there has been with 2,4,5-T, there is likely to be an upsurge in research activity. Dichlorprop, silvex, MCPA, and other phenoxy herbicides have received little attention in forest environment research; but their scope of use is limited and the data for their di- and tri- chlorinated phenoxyacetic acid relatives provide a reasonable basis for prediction.

In forest applications, phenoxy herbicides are distributed initially among 4 major compartments: air, vegetation, forest floor and soil, and water. Most of the herbicide ends up in the forest floor and soil. In all compartments, the phenoxy herbicides are relatively rapidly decomposed, and there appears to be little opportunity for substantial exposure to these chemicals. A fairly extensive data base is available to establish the specific levels of phenoxy herbicide likely to occur in any one location at a particular time after application.

TCDD, the highly toxic contaminant of 2,4,5-T and silvex, has also been intensively studied, but little of this work has been done in the forest. The initial levels and persistence of TCDD in specific forest compartments can be estimated from laboratory and field studies. Bioaccumulation of TCDD is expected to occur if organisms are exposed to a substantive, continuing source of TCDD, but it has not been detected (extensively) from normal patterns of herbicide use.

The most glaring deficiencies in the data base for the phenoxy herbicides involve (1) residues and fates of herbicides in air, (2) fates of herbicides in forest streams (including sediment and biota), and (3) residues and fates of TCDD in all forest compartments. Attention needs to be directed toward filling these gaps to insure that a complete data base is available for assessing the risks which may be associated with the use of these chemical tools by forest land managers.

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