Environmental Fate of 2,4-Dichlorophenoxyacetic Acid

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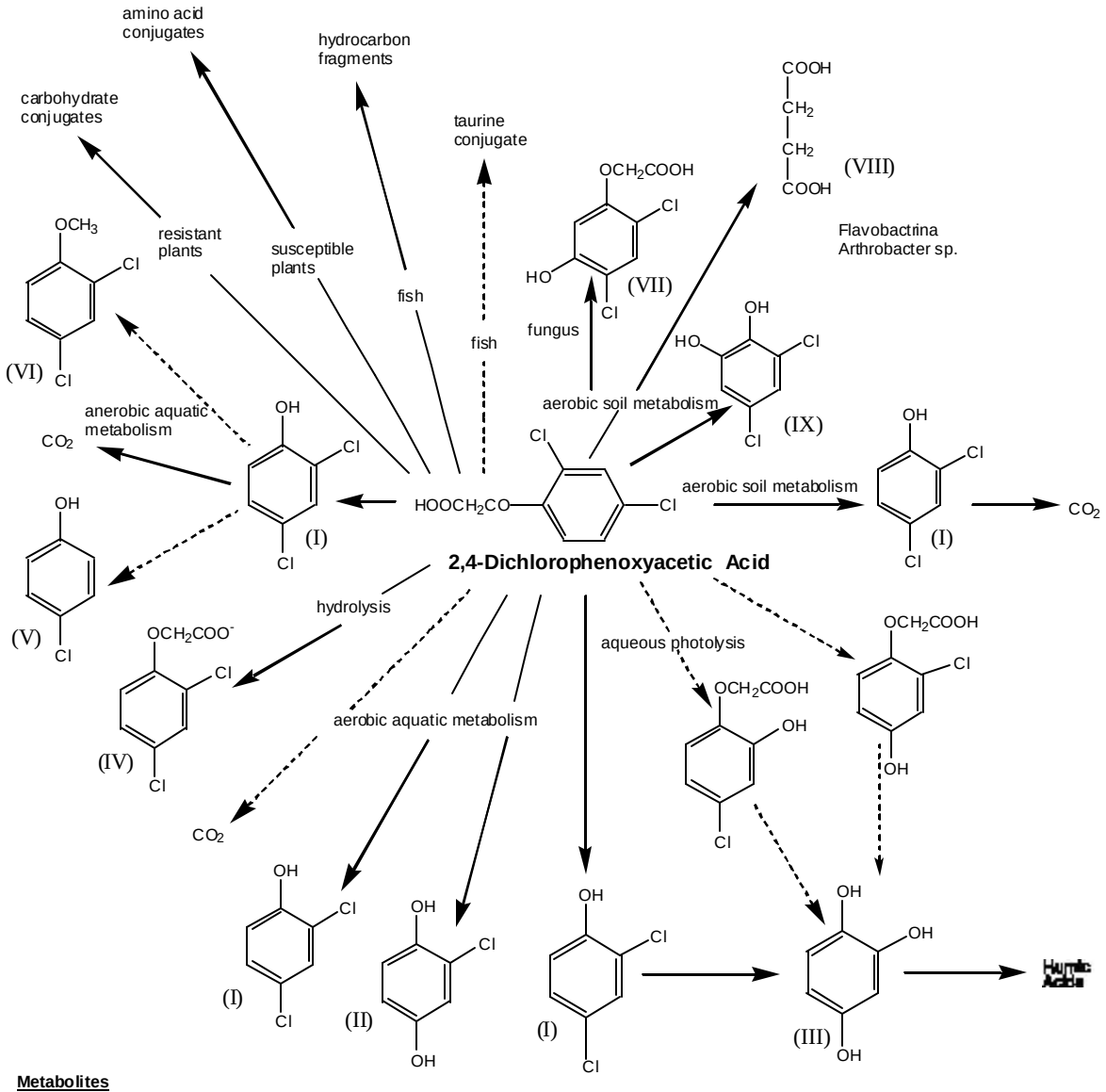
This document reviews the major routes of environmental fate for 2,4-Dichlorophenoxyacetic acid (2,4-D) with an emphasis and review of plant uptake, metabolism, and effects of exposure under forest conditions. 2,4-D is generally not applied as the acid, but is applied as one of several formulations. Due to the breakdown of the formulations to the 2,4-D acid, the acid will be discussed in this paper unless otherwise noted.

2,4-Dichlorophenoxyacetic Acid Degradation



Metabolites

(I) 2,4-Dichlorophenol (2,4-DCP)
(II) Chlorohydroquinone
(III) 1,2,4-Benzenetrionl
(IV) 2,4-D anion
(V) 4-Chlorophenol
(VI) 2,4-Dichloroanisol (2,4-DCA)
(VII) 2,4-Dichloro-5-hydrophenoxyacetic acid
(VIII) Succinic acid
(IX) 2,4-Dichlorocatechol

Figure 1

2,4-dichlorophenoxyacetic acid (2,4-D)

Table 1: Chemical characteristics of 2,4-D [a]

Molecular weight	221.04
Melting point[b]	135-142C
Boiling point (at .4 mmHg)[b]	160C
Water solubility (average of two values near 25C at pH7)	3.39×10^{4} ppm
Vapor pressure(at 25C)	1.4×10^{-7}mmHg
hydrolysis half-life (average of two values at 25C, pH7)	39 days
aqueous photolysis half-life (at 25C)	13.0 days
anaerobic aquatic half-life[c]	312 days
aqueous aerobic half -life[d]	15.0 days
aerobic half-life	66.0 days
soil photolysis half-life	393 days
field dissipation half-life	59.3 days
Henry's constant	1.76×10^{-12}
Octonal-water coefficient (Kow)[e]	9.15×10^{-2}-6.74×10^{2}
Soil adsorption coefficient (Koc) (data for four soil types)	0.067-1.1cm^3/g

a- Data from Kollman and Segawa (1995)
b- Data from EPA Pesticide Fact Sheet (1988)
c- Data from Concha and Shepler (1994)
d- Data from Cohen (1991)
e- Data from data package ABR-113698-E, DPR# 142-119

Table 2: Toxicity

Rat (acute, oral, male)[a]	639 mg/kg
Rat (acute, oral, female)[a]	764 mg/kg
Rat (acute, inhalation)[a]	1.79 mg/L
Rabbit (acute, percutaneous)[b]	LD_{50} >1600 mg/kg
Wild ducks (acute, oral)[b]	LD_{50} >1000 mg/kg
Japanese quail (acute, oral)[b]	LD_{50} 668 mg/kg
Pigeons (acute, oral)[b]	LD_{50} 668 mg/kg
Pheasants (acute, oral)[b]	LD_{50} 472 mg/kg
Dog[c]	LD_{50} 100 mg/kg
Chicken[c]	LD_{50} 540 mg/kg
not toxic to bees[b]	
Rainbow Trout (48 hour)[b]	LC_{50} 1.1 mg/l
Bluegill (48 hour)[d]	LC_{50} .9 mg/l
Striped bass (96 hour)[d]	LC_{50} 70 mg/l
Banded killfish (96 hour)[d]	LC_{50} 27 mg/l
Pumkinseed (96 hour)[d]	LC_{50} 65 mg/l
White perch (96 hour)[d]	LC_{50} 40 mg/l
American eel (96 hour)[d]	LC_{50} 300 mg/l
Carp (96 hour)[d]	LC_{50} 96.5 mg/l

Guppy (96 hour)[d] LC_{50} 70.7 mg/l
Dapnia magna (48 hour)[e] LC_{50} 1300 mg/l

a- Data from EPA Pesticide Fact Sheet (1988)
b- Data from The Agrochemicals Handbook, Third Edition (1991)
c- Data from Lilienfeld and Gallo (1989)
d- Data from Van Vakenburg (1969)
e- Data from data package 21447E AD 3-A, DPR# 142-091

Table 3: Comparison of 2,4-D Formulations

PROPERTIES	**LOW-VOLATILE ESTERS**	**HIGH-VOLATILE ESTERS**	**AMINE SALTS**	**AMINE SALTS**
FORMULATIONS USED IN FORESTRY	propylene glycol butyl ether ester, butoxy ethanol ester, isooctyl ester (2,ethylhexyl ester)	isopropyl ester, butyl, n-butyl, and isobutyl esters, ethyl ester	dimethylamine, triethanol amine, triisopropyl amine	dodecyl amine, tetradecyl amine, n-oleyl-1 amine, 3-propylene amine
SOLUBILITY	oil soluble	oil soluble	water soluble	oil soluble
USE	foliar sprays 80 to 90% of forest use	foliar sprays not used in forestry often due to volatility	cut surface or injection applications seldom used in forestry	foliar sprays used when low volatile esters not appropriate
FOLIAR ABSORPTION	readily adsorbed short chain alcohols may damage translocation mechanisms	readily adsorbed short chain alcohols may damage translocation mechanisms	poorly adsorbed uptake usually by roots	readily adsorbed
LEACHING POTENTIAL	not likely due to low water solubility	not likely due to low water solubility	more readily leached due to water solubility and polarity	not likely due to low water solubility
RUNOFF POTENTIAL	moderate potential	moderate potential	low potential	moderate potential
CHEMICAL DEGRADATION IN SOIL	converted to parent acid prior to degradation	converted to parent acid prior to degradation	converted to parent acid prior to degradation	converted to parent acid prior to degradation
CHEMICAL DEGRADATION WATER	hydrolyzed to the 2,4-D anion, rate is pH dependant	hydrolyzed to the 2,4-D anion, rate is pH dependant	dissociated to the anion	dissociated to the anion
VOLATILITY	low	high	negligible	negligible
ESTIMATED BIOCONCENTRATION FACTOR	medium to high estimated around 162-37,000 for the butoxyethanol and isooctyl esters, respectively	low estimated around 2.69 for isopropyl ester	low estimated around 0.1- 0.47 for the dimethylamine	

Based on information for forest formulations; other formulations exist for agricultural uses, but are not presented.

General Information and Mode of Action

2,4-Dichlorophenoxyacetic acid (2,4-D) is the active ingredient in several formulations of herbicides recommended for the control of broadleaf weeds. The major uses are on cereal crops such as wheat, corn, oats, rye, and barley, and the cane crops. It is also widely use to control dandelions and other broadleaf weeds in lawns, rangeland, and pastures. Other uses include the control of aquatic weeds, some woody vegetation, and site preparation and conifer release in forests.

Issues concerning the safety of 2,4-D center around its presence in the herbicide Agent Orange, a 1:1 mixture of 2,4-D and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T). Agent Orange, a herbicide widely used during the Vietnam war, was often contaminated with up to 40 mg/kg of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), a contaminant of the manufacture of 2,4,5-T, which has high potential to be carcinogenic, teratogenic, and fetotoxic (Lilienfeld and Gallo, 1989). Laboratory synthesis of 2,4-D does not produce any 2,3,7,8-TCDD. However, cross contamination did occur when facilities producing 2,4-D were also used to produce 2,4,5-T (Lilienfeld and Gallo, 1989). The registration for 2,4,5-T was suspended by the Environmental Protection Agency (EPA) in April 1978. 2,3,7,8-TCDD has never been detected by the EPA in any 2,4-D formulations that did not also contain 2,4,5-T, although trace levels of other relatively nontoxic dioxins may be present (Mullison, 1987; Munro *et. al.*, 1992).

2,4-D is generally applied to the foliage of broadleaf plants or directly to the soil as both a liquid or a granular product. It is also applied as an aqueous solution to sap-wood cuts in the bark known as a hack and squirt application. Plants absorb 2,4-D through their roots and leaves within 4-6 rain free hours after application (Munro *et al.*, 1992); if rain occurs, 2,4-D will dissolve in the rain water and runoff of plants and soil before sufficient amounts are absorbed by the plant. Following foliar absorption, 2,4-D progresses through the plant in the phloem, most likely moving with the food material. If absorbed by the roots, 2,4-D moves upward in the transpiration stream (EPA, 1988). Accumulation of the herbicide occurs in the meristematic regions of the shoots and roots. 2,4-D mimics the effect of auxins, or other plant growth regulating hormones, and thus stimulates growth, rejuvenates old cells, and overstimulates young cells leading to abnormal growth patterns and death in some plants (Mullison, 1987). Plants treated with 2,4-D often exhibit malformed leaves, stems, and roots. 2,4-D affects plant metabolism by stimulating nucleic and protein syntheses which affects the activity of enzymes, respiration, and cell division (EPA, 1988). Often, cells in the phloem of treated plants are crushed or plugged, interfering with normal food transport (Mullison, 1987) which can leave parts of the plant malnourished or possibly lead to death.

Most uses of 2,4-D in forests are for conifer release, site preparation, and right-of-way maintenance. The forest spray projects mostly utilize low volatile ester formulations of 2,4-D with a small proportion of amine salts also being used. Conifers are susceptible to damage during periods of rapid growth (Ghassemi *et al.*, 1981) and thus 2,4-D has limited use for seedling release in conifer forests. A typical label such as See® 2,4-D, an isooctyl ester with 61.74% active ingredient, recommends applying up to 3 quarts per acre of product before new growth on Douglas Fir is 2 inches in length and when 2/3 of the brush foliage has attained full sized leaves. To control susceptible brush species in Ponderosa Pine, the label recommends application of up to 3 quarts before pine growth begins in spring. This type of use may cause deformation of young needles in exposed firs which can be overcome in the years following spraying. The label also states that the product is toxic to aquatic invertebrates and should not be applied directly to water, to areas where surface water is present, or to intertidal areas below the mean high water mark.

Physical/ Chemical Properties

Pure 2,4-D can be found as flakes, powder, crystalline powder and solid material. It is white to light tan in color and may be odorless or have a phenolic aroma. The compound is stable to its melting point at 135-142ᴺ C (EPA, 1988). 2,4-D forms water-soluble salts with alkali metals and amines. Sequestering agents are usually added to prevent the precipitation of calcium and magnesium salts in hard water (The Agrochemicals Handbook, 1991). 2,4-D is soluble in most organic solvents and is insoluble in benzene and petroleum oils (EPA, 1988). However, the esters are soluble in oils (Meister and Sine, 1994) and are generally formulated as emulsions. Esters of low molecular weight alcohols have relatively high vapor pressures and will readily volatilize (USDA Forest Service, 1984). The 2,4-D salts are formulated as aqueous solutions.

Environmental Fate and Persistence of 2,4-D

AIR: Volatilization plays only a minor role in the breakdown and dissipation of the 2,4-D acid due to its low vapor pressure of 1.4×10^{-7} mmHg (Table 1). Further, there is little movement of 2,4-D acid through the air/water barrier, the barrier between atmosphere and surface water or soil moisture, into air due to a low Henry's Law Constant of 1.76×10^{-12}.

The primary source of 2,4-D in air is drift from spray applications of the herbicide (Howard, 1991). If proper application techniques are not used, the high volatile esters may be prone to spray drift causing toxic effects in nearby crops (Ghassemi *et al.*, 1981). With the exception of the high volatile ester formulations, the small amount of 2,4-D that gets into the air is subject to photooxidation by reaction with hydroxyl radicals with an estimated half life of 1day (Howard, 1991) or dissolves into water droplets and is transported back to the earth's surface via wet deposition (Ghassemi *et al.*, 1981). The low volatile ester and amine formulations are used in forests so drift from those applications is relatively negligible.

WATER: In the aqueous environment, 2,4-D is most commonly found as the free anion (Halter, 1980). The amine salt formulations dissociate to the anion and ester formulations hydrolyze to the anion, usually within one day (Ghassemi *et al.*, 1981). The rate of hydrolysis is pH dependent, with the hydrolysis half-life at pH 9 much shorter than the half-life at pH 6 (Ghassemi, *et al.*, 1981; Zepp *et al.*, 1975). Therefore, the persistence of the 2,4-D anion is of primary concern. Residues of 2,4-D can enter ponds and streams by direct application or accidental drift; by inflow of herbicide previously deposited in dry streambeds, pond bottoms, or irrigation channels; runoff from soils; or by leaching through the soil column (Norris 1981). Groundwater contribution of 2,4-D residues into ponds and streams is dependant upon soil type, with coarse-grained sandy soils with low organic content expected to leach 2,4-D into groundwater (Howard, 1991). Transport losses from forest soils to water bodies are expected to be less than losses from agricultural soils due to factors such as reduced surface runoff, adsorption to forest litter, absorption by plants, and possible greater organic material and microbial activity in forest soils (U.S.D.A Forest Service, 1984).

Decomposition of the anion appears to result from microbial or photodegradation, with photolysis playing a

minor role if microbial degradation is rapid. Both aerobic and anaerobic degradation are possible, although anaerobic degradation is relatively slow with a half-life of 312 days. In water, 2,4-D will biodegrade at a rate dependent upon the level of nutrients present, temperature, availability of oxygen, and whether or not the water has been previously contaminated with 2,4-D or other phenoxyacetic acids (Howard, 1991). Microbial degradation is a possible route for the breakdown of 2,4-D, but it is very dependent on the characteristics of the water. Laboratory studies have shown that in warm, nutrient rich water that has been previously treated with 2,4-D microbial degradation can be a major factor for dissipation (Halter, 1980). Natural surface waters are generally cool with nutrient concentrations less than those needed to maintain 2,4-D degrading microorganism populations (Ghassemi *et al.*, 1981). These conditions would not promote the growth of microorganisms needed to achieve microbial degradation. Microbial metabolism has been found to be biphasic with the first phase being a lag phase where the microbes acclimate to the test compound and the second phase being rapid metabolism with a total half-life of 15.0 days for both phases (Cohen, 1991). Cohen reports 2-chlorohydroquinone (1,4-dihydroxy 2-chlorophenol) as the major metabolite and 2,4-dichlorophenol and carbon dioxide as minor metabolites. Anaerobic aquatic metabolism is a minor pathway with a half-life of 312 days. Major metabolites are 2,4-DCP and carbon dioxide, with 4-chlorophenol and 2,4-dichloroanisol (2,4-DCA) as minor metabolites (Concha and Shepler, 1994).

2,4-D has an aqueous photolysis half-life of 13.0 days at 25E C at the surface of distilled water. In natural surface waters photodecomposition is not expected to be significant due to weaker ultraviolet radiation of natural sunlight and the presence of suspended and organic matter which reduces the effects of solar radiation (Ghassemi *et al.*, 1981). The half-life is expected to increase with depth due to reduction in penetration. According to a study by the Industry Task Force on 2,4-D, the major photodegradation product is 1,2,4-benzenetriol (Cohen and Tamma-Vithala, 1989). Additional studies showed that 2,4-D is susceptible to photodegradation resulting in the formation of carbon dioxide, 1,2,4-benzenetriol, 2,4-dichlorophenol and then proceeds to a secondary photolysis forming humic acids (Crosby and Tutass, 1966; Hautala, 1978*)*.

For high volatile ester formulations of 2,4-D, volatilization may play a larger role for removal from water than hydrolysis. In neutral and acidic waters conversion from ester to anion via hydrolysis is slower than the potential rate of vaporization (Ghassemi *et al*., 1981).

SOIL: In soil, 2,4-D esters and salts are first converted to the parent acid prior to degradation. The rate of the ester hydrolysis decreases with decreasing soil moisture and with increasing molecular weight of the alcohol portion of the ester. The fate of 2,4-D may be affected by several processes including runoff, adsorption, chemical and microbial degradation, photodecomposition, and leaching. Water solubility and the soil adsorption coefficient (K_{oc}) indicate the potential mobility of a chemical in soil; while the aerobic and anaerobic soil metabolism, hydrolysis half-lives, and field dissipation rate indicate the persistence of a chemical in soil (Linde, 1994). 2,4-D has a moderate persistence in soil with a field dissipation half-life of 59.3 days, aerobic half-life of 66 days, and a hydrolysis half-life of 39 days (Table 1). Hermosin and Cornejo (1991) reported that by using a simple regression analysis between adsorption capacities and soil properties, they found that high organic matter and free iron in soils favored the adsorption of 2,4-D, while high pH, large surface area, and phyllosilicates as essential clay components decreased adsorption (Hermosin and Cornejo, 1991). 2,4-D is in nonionic form at pH less than 6 and is in anionic form at pH greater than 6. In slightly acidic soils, 2,4-D will be adsorbed at pH less than 6 but will not be adsorbed as

much if in the anionic form because the negative charges of the soil and chemical repel each other (Hillel, 1982).

Microbial degradation is considered to be the major route in the breakdown of 2,4-D in soil. The most important mechanism of microbial degradation involves the removal of the acetic acid side chain to yield 2,4-DCP. This is followed by ring cleavage and degradation to produce aliphatic acids such as succinic acid (Ghassemi *et al*., 1981). The rate of microbial degradation is dependent upon the water potential, depth and temperature of the soil. Han and New (1994) found that sandy loam soil containing 2,4-D degrading single-celled bacteria, filamentous bacteria (actinomycetes), and fungi had the lowest degradation rates at a low water potential of -5.5 MPa (megapascals), with -0.1MPa corresponding to soils at or below field capacity. An increase in water potential resulted in increased rates of breakdown up to an optimum at -0.1 MPa (Han and New, 1994). Dry soil conditions contribute to the inhibition of 2,4-D mineralization by restricting solute mobility, reducing the herbicide degrading activity of organisms, and suppressing the 2,4-D degrading microorganism populations. Under dry conditions the addition of organic matter may enhance degradation by simulating the co-metabolizing fungal and actinomycete communities (Han and New, 1994). The rate of microbial degradation is also dependent on soil depth and temperature, with rates of degradation decreasing with increased depths and lower temperatures (Veeh *et al.*, 1996).

Degradation in soil is affected by the rate of adsorption-desorption of 2,4-D onto soil particles which bind the chemical, making it unavailable for microbial degradation (Bolan and Baskaran, 1996). Bolan and Baskaran found that as soil organic carbon content increased to 12 % the rate of adsorption increased correlating to a decreased rate of degradation due to low concentrations of 2,4-D available for microbial degradation. But when the organic carbon content was more than 12% there was an increase in the rate of both adsorption and degradation. The enhanced degradation of 2,4-D was attributed to the increased biological activity of the soil and the decreased 2,4-D-induced inhibitory effect on microbial activity (Bolan and Baskaran, 1996). Benoit *et al*. have also demonstrated the importance of soil organic matter in the sorption of 2,4-D. Lignin from plant tissue or aliphatic compounds from microbial origin contributed to increased sorption, while compounds such as soluble tannins decreased sorption (Benoit *et al.*, 1996). This indicates that the addition of lignin or aliphatic compounds to soil may decrease the rate of degradation, while the addition of soluble tannins may increase the rate of degradation.

Photodecomposition on soil surfaces plays a very minor role in the breakdown of 2,4-D and only occurs on the upper surface of the soil. In a photolysis study conducted by the Industry Task Force on 2,4-D, no degradation products were found at concentrations above 1.1% of the initially-applied compound indicating that 2,4-D is very resistant to soil photodegradation (Tamma-Vithala, 1989). Another study conducted by the EPA was unsuccessful in identifying the photodegradation products (Hautala, 1978). In both studies it was thought that the potential major soil photodegradation products would be 2,4-dichlorophenol, 1,2,4-benzenetriol, and 2-chlorohydroquinone.

The high water solubility of 4.46×10^4 ppm and low soil adsorption coefficient of 0.067-1.1 cm^3/g for the 2,4-D free acid suggest that it has a high potential to leach in soil. The principle means of movement would probably be with percolating water, while diffusion is important only for transport over small distances (Howard, 1991). The adsorption capacity of a given soil affects the potential for leaching of 2,4-D; in soils that promote adsorption, the leaching potential is lower. As discussed previously, 2,4-D

adsorption has been correlated with the organic content. Grover (1977) found that higher volumes of water were required to leach 2,4-D from soils with a high organic content. Further, leaching was correlated with the pH of soils; 2,4-D leached more readily in soils with pH's of 7.5 and above (Grover, 1977) reflecting higher adsorption to organic matter in more acidic soils (Hillel, 1982). However, despite its potential mobility, 2,4-D generally remains within the top few inches of the soil (Ghassemi *et al.* 1981). Stearman and Wells (1997) found that most of the 2,4-D, applied at a rate of 4.49 kg/ha in the ester form to nursery plots with varying crop covers, remained in the top 20 cm of the soil. Norris (1981) states that entry via leaching is not an important process for transporting significant quantities of 2,4-D into streams since it is adsorbed onto organic material and is readily degraded by microorganisms.

The extent of leaching and runoff of 2,4-D is influenced by the formulation, soil properties, slope, and timing and intensity of rainfall. 2,4-D was found susceptible to runoff if the rain event occurred shortly after the application, with runoff concentrations decreasing over time (Stearman and Wells, 1997). According to Norris (1981), runoff is relatively uncommon on most forest sites because forest soil has a very high infiltration capacity and is overlain by a litter and humus layer. Meru *et al.* (1990) found that 2,4-D did not have a significant tendency to move laterally within the soil downslope from treated areas under 60 to 297 mm of rainfall for Minden, Ontario and 60 to 257 mm of rainfall for Acton, Ontario during summer and fall. When compared to triclopyr, 2,4-D has been found to be slightly more mobile in three soil systems; paddy rice soil, rain-fed lowland rice, and bareground soil, although 2,4-D was found to dissipate at a rate faster than triclopyr (Johnson *et al.* 1995). Dissipation of 95% of the initial concentration (DT_{95}) in paddy rice soil, rain-fed lowland rice, and bareground soil of 2,4-D was 15, 26, and 20 days respectively, while DT_{95} of triclopyr was 20,>49, and >49 days respectively (Johnson *et al.* 1995). As a result of thin-layer chromatography studies finding 2,4-D mobile in silty clay loam soil at pH 6.8, the compound has been placed in mobility class IV, relatively mobile, with the metabolites found to be less mobile (Helling, 1971). Since esters do not leach into soil as readily as the more soluble formulations, they have a greater potential to be carried in surface runoff (Ghassemi *et al.*, 1981). Wilson and Cheng (1976) studied the isooctyl ester and dimethylamine salt formulations of 2,4-D and found that both formulations are subject to similar surface runoff within a few days after application if sufficient rainfall occurs.

Biota:

Plants: In plants, 2,4-D formulations having high lipid solubility (such as the esters) rapidly penetrate the cuticle. An oil carrier is usually added to water soluble formulations to enhance penetration. Salt formulations are most readily absorbed through the roots, while esters are more readily absorbed through foliage. Foliar applied 2,4-D is easily translocated in the phloem and carried with material from photosynthesizing leaves to growth sites where it accumulates. Translocation of 2,4-D upward by roots takes place primarily in the transpiration stream of the xylem (Loos, 1975). The rate of translocation of the compound is affected by environmental conditions such as soil moisture and atmospheric humidity (USDA Forest Service, 1984). 2,4-D mimics the effects of auxins (plant growth regulators) and is found to persist in plant tissues longer than the natural hormone. Ester formulations do not function as growth regulators until they are converted to the acid form, usually within ½ hour after application (USDA Forest Service, 1984). The immediate cause of plant death is due to abnormal metabolism of nucleic acids (USDA Forest Service, 1984). Plants metabolize 2,4-D by degradation of the side chain, hydroxylation of the ring structure (addition of OH^-), conjugation of 2,4-D with plant constituents, formation of metabolites, ring cleavage, or side chain lengthening (Loos, 1975). 2,4-D resistant plants convert the chemical into

inactive, nontoxic carbohydrate conjugates, while susceptible plants convert it into amino acid conjugates which obstruct normal nucleic acid metabolism and protein synthesis (Ghassemi *et al.*, 1981; USDA Forest Service, 1984).

Mammals: 2,4-D enters mammals via inhalation, ingestion, or through the skin. 2,4-D is not metabolized in mammals but is rapidly eliminated via the kidneys and excreted with the urine as the parent compound. The half-life in humans is 17.7 hours (USDA Forest Service, 1984). Due to its high solubility, 2,4-D is carried in blood and interstitial tissues through the gut and kidneys, but does not accumulate in any tissues (Munro *et. al.*, 1992). An exception are the 2,4-D esters which are hydrolyzed to the acid prior to adsorption. Once converted to the acid in mammalian systems, 2,4-D exists predominantly in the ionized form at physiological pH, is not metabolized to reactive intermediates, and does not readily cross lipid membranes into tissues without active ion transport systems (Munro *et. al.*, 1992).

In the mammals studied, 2,4-D is considered mildly toxic with LD_{50}'s ranging from greater than 1600 mg/kg in rabbits to 472 mg/kg in pheasants. Symptoms of exposure include gastrointestinal disturbances, weight loss, muscle weakness, and loss of coordination. In addition, some formulations cause eye, skin and respiratory irritation. The salts and esters have been found to have approximately the same toxicity as the acid, although solvents can effect toxicity.

Fish: The effect of 2,4-D on fish depends on the formulation and the age and species of fish. The bioconcentration factor (BCF, a ratio of the test substance concentration in fish to the concentration in water) for 2,4-D ranges from an estimated 7 for the acid to an estimated 37,500 for the isooctyl ester to an estimated 0.1 to 0.47 for the dimethylamine salt (Howard, 1991).
2,4-D when applied as the acid shows little tendency to bioconcentrate in fish while if applied as the isooctyl ester it is expected to bioconcentrate in the absence of metabolization. In fish, accumulated 2,4-D is rapidly broken down into hydrocarbon fragments which are utilized by the fish for synthesis of normal body tissue and/or eliminated (Ghassemi *et. al.*, 1981). In trout 72 ± 4% of 2,4-D is excreted via urine as the unchanged acid within 8 hours after exposure with a half-life of 2.4 hours (Carpenter and Eaton, 1983).

Subacute toxicity tests showed that 2,4-D induced changes in the enzyme activities and morphological changes in the gills, liver, and kidneys of adult fish (Neskovic *et. al.*, 1994). A toxicity study done on Salmonids in southeast Alaska showed that the butyl ester was the most toxic of the ester formulations and the isooctyl ester was the least toxic. 100% mortality occurred for pink, chum, and coho fry exposed to 1 ppm 2,4-D butyl ester and sockeye smolts, dolly varden, rainbow and Oregon coho fingerlings exposed to 5 ppm 2,4-D butyl ester (Meehan *et al.*, 1974). The no-effect level was less than 1ppm, but not more precisely described. The same study also found the no-effect level for isooctyl ester to range from 1ppm to 10 ppm for all the same fish species except for pink salmon fry and sockeye smolts which showed 40 and 6.7% mortality at 1ppm, respectively. The pure acid form of 2,4-D at 1ppm only showed high mortality in the pink fry (Meehan *et al.*, 1974).

Studies Relating to a Forest Environment

Wu, Ching Chen *et al.* (1971). The effects of 2,4-D on histological changes of red pine (*Pinus resinosa*) were studied at concentrations of 50 and 100 ppm. Petri dishes, containing filter paper and 50

red pine seeds, were prepared with 100 or 50 ppm of 2,4-D or distilled water as a control. The dishes were placed in a growth chamber and maintained at constant temperature and light intensity. Dishes for the 100 ppm treatment were removed at days 2, 3, 4, 5, 6, 7, 9, 12, 15, and 18 and dishes for the 50 ppm treatment were removed at days 12, 15, and 18.

Both dosages of 2,4-D altered seedling development with no clear differences between the two concentrations observed. In root development, cell division and elongation of treated plants had stopped after 6 days. At 12 to 18 days, the roots lacked a well-defined endodermis. 2,4-D did not significantly retard increase of above ground tissue, but at 9 days guard cells that were present in control plants were not present in treated ones. At 12 days, a marked difference in the size and development in tissues of shoots appeared between control and treated plants. Abnormal thickening of the shoot and cotyledon was found in all 2,4-D treated plants as a result of proliferation and expansion of parenchyma cells. Parenchyma and cortical cells multiplied rapidly and produced small cells with large nuclei and dense cytoplasm, while the xylem, phloem, and epidermal cells were not stimulated. Collapse of the parenchyma cells in the upper stem was followed by callus tissue formation. Two general patterns of cell divisions occurred; cells either divided in randomly oriented planes or in radial series. In the cotyledon, mesophyll cells were enlarged with division and expansion of cells progressing from the cotyledonary node toward the apex at 6 days. At 12 days, a well-defined endodermis was lacking, the numbers of stomata and chloroplasts were low, and cotyledons were fused to primary needles. The authors concluded that red pine seeds treated with 50 to 100 ppm of 2,4-D will exhibit a lower growth rate and planting quality of seedlings.

Gratkowski, H.J. (1978) studied the possibility of late winter as an alternative season to control greenleaf manzanita without damaging intermingled ponderosa pines (*Pinus ponderosa*). Trees in the treatment area were 1 to 2 meters tall at the time of treatment; manzanita shrubs were 1 to 1½ meters tall. Water and oil-in-water emulsion carriers were used. Trees and manzanita were sprayed on eight dates beginning in late November 1969 and ending late May 1970. The pine trees were sprayed to drip point with 0.5lb acid equivalent per 100 gal and manzanita was treated with 2.5lb per 100 gal. Phenological descriptions of both pine and manzanita were recorded for each spray date.

Greenleaf manzanita was highly susceptible to 2,4-D throughout the study period, with all shrubs killed regardless of treatment date. The susceptibility of ponderosa pine changed throughout the treatment. No damage occured in trees sprayed prior to February. In mid- February, three months before the spring flush of growth, ponderosa pine became susceptible to damage from 2,4-D. This susceptibility coincided with the blooming of the first flowers on manzanita. Damage to pine trees was most severe for sprays applied in late May at the beginning of spring growth. Gratkowski combined these data with similar data from another study and concluded that ponderosa pine was not damaged by foliar sprays of 2,4-D in water or emulsion carriers applied during September, November, or January.

Otta, J.D. (1974) studied the effects of 2,4-D exposure on Siberian elms. Three year old elms that had been planted in Brookings, South Dakota the previous year were used as the test subjects. A commercial source of the dimethylamine salt of 2,4-D was used to treat elms with concentrations of 0 (water control), 3, 5, 10, 25, 50, and 100 ppm 2,4-D acid equivalent. 2,4-D was applied at each treatment concentration in June of 1972. Ten days after application, the 3, 5, 10, and 25 ppm treatments exhibited leaf cupping and twig distortion. The 50 and 100 ppm treatments caused severe leaf scorching followed by the death of

small twigs 25-30 cm back from the tips. Some regrowth occurred in late summer for all treatments. One year after the 2,4-D applications, all trees, except 0 and 3 ppm treatments, showed injury on the first foliage produced. Treatments of 5 ppm and above resulted in leaf cupping, treatments of 10 ppm and above showed significant reduction in growth up to 68% in the 100 ppm treatments. Concentrations of 25, 50, and 100 also caused bark abnormalities significantly different from the other treatments.

Newton *et al.* (1990). This study researched the deposition patterns, persistence, and mobility of 2,4-D, triclopyr, and picloram applied aerially to brush in southwestern Oregon. 2,4-D, formulated as the propylene glycol butyl ether ester, was applied at rates of 3.3 kg/ha and 2.2 kg/ha. Each treatment was applied to one plot at three different sites. Foliage, litter, and soil residues were reported as the whole-plot mean. The three sites were chosen for their similar vegetation but varying precipitation. Tanoak bushes were chosen for vegetation sampling because they provided the most consistent plant material in the three sites.

Crown (> 90 cm above ground) and browse (30-90 cm above ground) foliage samples were collected from pre-tagged branches on days 1, 18, 37, 79, 153, and 325 (except browse samples). Initial concentrations of 2,4-D in browse foliage was about one-third that of the crown, with litter concentrations slightly higher than in browse foliage. For the 3.3 kg/ha application, half-lives for the crown, browse, and litter were 234.7, 36.9, and 127.0 days respectively. The half-lives for the 2.2 kg/ha application were 57.6, 28.8, and 18.9 days for crown, browse, and litter. The herbicide killed the leaves slowly with wilting occurring over several months. After initial losses, 2,4-D was found to persist in evergreen foliage and twigs. In litter, concentrations decreased quickly, but then rose slightly the next spring as new residues fell from the crowns.

Thirty to 50% of 2,4-D remained in the dry surface soil 37 days after the application. This suggested that some mechanism other than microbial degradation was responsible for a majority of the loss from day 1 to 37. The greatest decrease of 2,4-D in the soil occurred from 37 to 79 days after treatment correlating with a warm, moist period. The half-lives at this time ranged from 11 to 25 days. Soil samples showed no movement from up-slope treatment suggesting that movement by subsurface flow was negligible.

Entry *et al.* (1995) tested the age of riparian forests on atrazine and 2,4-D degradation in soils of the Oregon Coast Range. Three riparian sites supporting forest ecosystem vegetation of three ages were selected : young growth (20-40 years), second growth (60-90 years), and old growth (120-3– years). The litter layer and the top 10 cm of mineral soils at three locations were sampled three times per season in forests of each age. Samples were measured for microbial biomass and herbicide degradation. In mineral soil, neither the active and total fungal biomass nor the active and total bacterial biomass differed with forest age or season. However, in litter the active fungal biomass was greater in old-growth samples than in those from younger forests in both spring and fall. Active fungal biomass was also greater in both old- and second-growth than in young-growth samples in winter. Active bacterial biomass in litter did not differ with age in summer or winter, but was greater in spring and fall on old-growth samples. In all season except winter, 2,4-D mineralization was greater in old- and second-growth litter, and in old-growth soils mineralization was greater than both second- and young-growth soils. Mineralization in litter and soil was lowest in winter for forest ages. This study indicated that as forest ecosystems mature, the rate of degradation of 2,4-D in litter and soil increases.

Summary

2,4-dichlorophenoxyacetic acid is a hydrophilic compound that tends to remain in water and not adsorb onto soil. Volatilization into air is considered negligible for most formulations except for the high volatile esters. In water, the acid hydrolyzes to the 2,4-D anion and is subject to microbial degradation as the major route of degradation with rates increasing in soils that have been previously treated with the herbicide. 2,4-D is not considered persistent in soil since it tends not to adsorb onto soil unless high levels of organic carbon are present. The compound is relatively mobile, but due to rates and types of applications (usually foliar) along with the relatively high rate of microbial degradation 2,4-D is not likely to leach into subsurface flow. 2,4-D has little tendency to bioconcentrate in animal tissue and is usually excreted unmetabolized via urine except for some of the low-volatile esters which will bioaccumulate in the absence of metabolization (Howard, 1991). Some formulations, especially the butyl ester, can be highly toxic to fish. In humans, 2,4-D acid is largely excreted unchanged with no evidence of accumulation in tissues or metabolization to reactive metabolites.

Sampling results for 2,4-D contained in DPR's surface water database, as of 7/27/99. Results are given in parts per billion (ppb).				
study no.	sampling site	sample date	conc	rpl
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	3-Mar-92	0.1	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	6-Mar-92	2.78	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	10-Mar-92	0.1	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	13-Mar-92	0.67	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	17-Mar-92	2.1	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	20-Mar-92	0.4	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	24-Mar-92	0.26	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	27-Mar-92	0.26	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	31-Mar-92	0.46	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	3-Apr-92	0.1	0.1
6	Colusa Basin Drain at Rd. 99E, near Knights Landing	7-Apr-92	0.63	0.1
6	Sacramento River 0.4 km upstream from Colusa Drain Basin	13-Mar-92	0.1	0.1
6	Sacramento River 0.4 km upstream from Colusa Drain Basin	17-Mar-92	0.2	0.1
6	Sacramento River at I Street Bridge	6-Mar-92	0.1	0.1
6	Sacramento River at I Street Bridge	17-Mar-92	0.1	0.1
6	Sacramento River at I Street Bridge	14-Apr-92	0.1	0.1
6	Sacramento River at Knights Landing Br. on Hwy. 11	6-Mar-92	0.1	0.1
6	Sacramento River at Knights Landing Br. on Hwy. 11	17-Mar-92	0.1	0.1
6	Sacramento River at Tower Bridge	6-Mar-92	0.1	0.1
6	Sacramento River at Tower Bridge	17-Mar-92	0.1	0.1
6	Sacramento River at Tower Bridge	14-Apr-92	0.1	0.1
6	Sutter Bypass at Karnak Pumping Sta.	13-Mar-92	0.1	0.1
6	Sutter Bypass at Karnak Pumping Sta.	17-Mar-92	0.3	0.1
6	Sutter Bypass at Karnak Pumping Sta.	20-Mar-92	0.2	0.1
6	Sutter Bypass at Karnak Pumping Sta.	24-Mar-92	0.1	0.1
30	Colusa Basin Drain #5	11-Jun-96	0.32	0.1
30	Colusa Basin Drain #5	13-Jun-96	0.73	0.1
30	Colusa Basin Drain #5	18-Jun-96	0.1	0.1
31	Sutter Bypass 1 mi. south Hwy. 20	26-Jun-97	0.1	0.1
40	Colusa Basin Drain #5	30-Jun-98	0.25	0.1
40	Colusa Basin Drain #5	7-Jul-98	0.11	0.1
41	Arcade Creek at Norwood	10-Apr-97	0.26	0.035
41	Arcade Creek at Norwood	11-Jul-97	0.16	0.035
41	Arcade Creek at Norwood	29-Aug-97	0.46	0.035
41	Arcade Creek at Norwood	5-Sep-97	0.16	0.035
41	Arcade Creek at Norwood	7-Nov-97	0.42	0.15
41	Arcade Creek at Norwood	9-Mar-98	0.14	0.15
41	Arcade Creek at Norwood	23-Apr-98	1.39	0.15
41	Colusa Basin Drain at Rd. 99E, near Knights Landing	18-Feb-97	0.14	0.035

41	Colusa Basin Drain at Rd. 99E, near Knights Landing	18-Mar-97	0.78	0.035
41	Colusa Basin Drain at Rd. 99E, near Knights Landing	26-Feb-98	0.11	0.15

Study 6: DPR study EH95-11
Study 30: DPR 1996 rice pesticide monitoring program
Study 31: Sutter County Department of Agriculture
Study 40: DPR 1998 rice pesticide monitoring program
Study 41: USGS NAWQA data 1996-1998

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