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Fate of Xenobiotics in Foliar Pesticide Deposits

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I. Introduction

The environmental fate of pesticides and other xenobiotic materials initially within pesticide deposits on foliage has received little holistic study. Spencer et al. (1973) noted that there has been extensive research on volatilization from soils, but little has been directed at residues on foliage. Although other investigators note herbicide volatilization from foliage is the primary source of residues that cause downwind damage to susceptible crops (Thompson 1983), there is still little data and theoretical development of this topic. In a recent review of photodegradation of herbicides, the subject of photodegradation occurrence in deposits on leaf surfaces is not mentioned (Marcheterre et al. 1988). A recent review of the persistence of pesticides on foliage not only summarizes the many studies that have contributed information to this area, but also stresses that most studies

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of pesticides on foliage are highly empirical and do not define the mechanisms of residue dissipation (Willis and McDowell 1987).

The persistence of pesticides in foliar deposits is important in assessments of field worker exposure to pesticides. The combined dissipative and degradative (dispositional) processes that operate on a material in a spray deposit on foliage determine the quantity of dislodgable residues remaining at different times after application. Dislodgable residue quantities are important in determining the potential dermal exposure of workers who reenter fields (Iwata 1980; Knaak 1980). Reentry intervals are useful values for protecting field workers from toxic exposures.

The chemical environment of foliar deposits is unique in its complexity. Plant cuticles are a complex mixture of long-chain esters, aldehydes, ketones, and alcohols (Baker 1980; Chamel 1986). These materials assume different physical shapes, such as plates or needles, that are characteristic of particular plant species. A spray deposit consists of a complex mixture of the pesticidal compound, pesticide synthesis contaminants, surfactants, solvents, occasionally clays, and other adjuvants.

The meteorological environment has a strong influence on the dissipation and degradation of xenobiotic substances in foliar pesticide deposits. Meteorological conditions often change rapidly and randomly. Temperature is a measure of the heat in a system that drives diffusive phenomena and influences the rate of chemical reactions. Humidity and plant-moisture relations are strongly influenced by heat, but also may be subject to random fluctuations. Insolation both drives some dissipative processes by the addition of thermal energy and reduces the quantity of susceptible compounds in a deposit via photodegradation (Choudry and Webster 1985; Crosby 1976; Marcheterre et al. 1988). Deposits are subject to widely different levels in insolative flux as a result of canopy structure, diurnal patterns, and clouds.

An extensive amount of work has focused on the fate of pesticides in the soil, air, and water environments. Many reviews of processes that occur in these environments are available (Choudry and Webster 1985; Jury et al. 1987; Laskowski et al. 1983; Marcheterre et al. 1988; Smith et al. 1983; Spencer et al. 1973; Suntio et al. 1988; Swann et al. 1983; Woodrow et al. 1983). But there are few reviews specifically addressing the disposition of pesticides in foliar deposits (Ebeling 1963; Quistad and Menn 1983). This review bridges this gap in the literature, and provides an overview of the information on xenobiotic substance dynamics in relation to pesticide deposits on foliage.

The objectives of this review are:

1. To review research approaches used to characterize the volatilization, photodegradation, and foliar penetration of pesticides.
2. To identify limitations of these research approaches with respect to (a) actual deposit composition; (b) utility of the data for environmental fate modeling;

(c) interactions between processes; (d) influence of environmental conditions, such as temperature, humidity, and insolation on pesticide dissipation and degradation; and (e) the usefulness of the data for risk assessments.

3. To develop a mechanistic perspective on the processes involved with the disposition of substances in pesticide deposits on foliage.
4. To discuss approaches to modeling the fate of chemicals in pesticide deposits on foliage.

The major processes affecting residues in pesticide deposits on foliage (besides washoff by rain) are foliar penetration, volatilization, and photodegradation. In the following sections, the traditional approaches for studying these processes are evaluated. A conceptual framework for the generation of hypotheses on the influence of these processes and other factors on the fate of residues in pesticide deposits on foliage is presented.

II. Foliar Penetration

Most investigations of foliar penetration (absorption) have concerned herbicides, because the absorption of an herbicide into leaves is a prerequisite for their eventual efficacy. A few studies have explicitly looked at foliar penetration by insecticides (Makary et al. 1981; Sarode and Rattan 1982; Takahashi et al. 1985).

Two general designs have been used to study foliar penetration. Most common are empirical studies of foliar absorption, usually used as part of a broader study of foliar penetration, translocation, and metabolism of herbicides. The other approach has been to isolate plant cuticles and determine the rate of pesticide diffusion through the cuticle. This approach is predicated on the belief that foliar penetration is solely a function of cuticular composition and structure.

A literature search for 1977 through 1988 produced the studies shown in Table 1. The studies have been categorized according to the processes and factors that were considered in the protocols. Table 1 is a survey showing the different amount of attention given to various critical aspects, in terms of environmental fate, of foliar penetration of pesticides from deposits.

A. Empirical Foliar Penetration Studies

1. Plant Materials. In empirical foliar penetration studies, whole plants, usually seedlings, are used as the experimental substrates. The plants are either crops, target weeds, or a combination of both, to which the pesticide is commonly applied. The plants are frequently grown in greenhouses or growth chambers (Table 1). Rarely are field-grown plants used as experimental materials. Baker (1980), in a review of the effects of cuticular components on herbicide absorption, indicates many studies show that plant growth environment has an influence on leaf cuticular structure and development. Therefore, penetration of an herbicide or other substance into foliage of a greenhouse- or growth chamber-

Table 1. A survey of foliar penetration studies; conditions and factors investigated that bear on the environmental fate of herbicides deposited on foliage.

Factor or process	Observation	References
Metabolism/ translocation	Measured	Akey and Morrison (1983); Baker and Hunt (1988); Bloomberg and Wax (1978); Bovey et al. (1983); Bovey et al. (1987); Caseley and Coupland (1980); Devine and Vanden Born (1985); Gillespie and Miller (1983); Haderlie (1980); Hamburg and McCall (1988); Hashimoto et al. (1979); Hogue (1978); Hook and Glenn (1984); Jordan (1977); Kells et al. (1984); Kitchen et al. (1980); McCall et al. (1986a); McCall et al. (1986b); Muller et al. (1984); Norris and Freed (1966); Nomura and Hilton (1982); O'Sullivan and Kossatz (1984); Petersen and Swisher (1985); Peterson et al. (1985); Reddy and Bendixen (1988); Richardson (1975); Richardson and Grant (1977); Richardson (1979); Richardson (1980); Ritter and Coble (1981); Schultz and Burnside (1980); Sharma et al. (1978); Shaner and Robson (1985); Taylor et al. (1981); Todd and Stobbe (1977); Veerabhadraiah et al. (1980); Waldecker and Wyse (1985); Wills (1978); Wills (1984); Wills and McWhorter (1981)
Environmental fate	Measured	Bentson (1989); Bovey et al. (1983); Caseley and Coupland (1980); Hamburg and McCall (1988); McCall (1988); McCall et al. (1986a); McCall et al. (1986b)
	Suspected effects	Babiker and Duncan (1975); Bovey et al. (1987); O'Sullivan and Kossatz (1984)
Temperature	Different levels	Bentson (1989); Gillespie and Miller (1983); Jordan (1977); Kells et al. (1984); McCall (1988); McCall et al. (1986a); McCall et al. (1986b); McWhorter and Wills (1978); McWhorter et al. (1980); Schultz and Burnside (1980); Sharma and Vanden Born (1970); Sharma et al. (1978); Taylor et al. (1981); Willingham and Graham (1988); Wills (1978); Wills (1984); Wills and McWhorter (1981)
Humidity	Different levels	Gillespie and Miller (1983); Babiker and Duncan (1975); Jordan (1977); McWhorter

Table 1. (*Continued*)

Factor or process	Observation	References
Humidity (cont.)		and Wills (1978); McWhorter et al. (1980); Sharma and Vanden Born (1970); Taylor et al. (1981); Willingham and Graham (1988); Wills (1978); Wills (1984); Wills and McWhorter (1981)
Time course Babiker	Different times	Akey and Morrison (1983); Duncan (1975); Baker and Hunt (1988); Bentson (1989); Bloomberg and Wax (1978); Bovey et al. (1983); Bovey et al. (1987); de Ruiter et al. (1988); Devine and Vanden Born (1985); Eberlein and Behrens (1984); Gillespie and Miller (1983); Haderlie (1980); Hamburg and McCall (1988); Hashimoto et al. (1979); Hook and Glenn (1984); Kells et al. (1984); Kitchen et al. (1980); McCall (1988); McCall et al. (1986a); McCall et al. (1986b); McWhorter and Wills (1978); McWhorter et al. (1980); Muller et al. (1984); Nomura and Hilton (1982); O'Sullivan and Kossatz (1984); Reddy and Bendixen (1988); Richard and Slife (1979); Richardson (1975); Richardson and Grant (1977); Richardson (1979); Richardson (1980); Riederer and Schonherr (1985); Ritter and Coble (1981); Schultz and Burnside (1980); Shafer and Bukovac (1988); Sharma and Vanden Born (1970); Sharma et al. (1978); Shaner and Robson (1985); Todd and Stobbe (1977)
	Approaches steady state	Akey and Morrison (1983); Baker and Hunt (1988); Bentson (1989); Bloomberg and Wax (1978); Caseley and Coupland (1980); Devine and Vanden Born (1985); Eberlein and Behrens (1984); Haderlie (1980); Hamburg and McCall (1988); Hashimoto et al. (1979); Hook and Glenn (1984); Kells et al. (1984); McCall (1988); McCall et al. (1986a); McCall et al. (1986b); McWhorter and Wills (1978); McWhorter et al. (1980); Nomura and Hilton (1982); Richardson (1975); Richardson (1979); Richardson (1980); Schultz and Burnside (1980); Shafer and Bukovac

Table 1. (*Continued*)

Factor or process	Observation	References
Time course (cont.)		(1988); Sharma and Vanden Born (1970); Todd and Stobbe (1977)
Surfactants/ adjuvants	Comparisons	Babiker and Duncan (1975); de Ruiter et al. (1988); Haderlie (1980); Hamburg and McCall (1988); McCall et al. (1986b); Peterson et al. (1985); Shafer and Bukovac (1988); Willingham and Graham (1988); Zabkiewicz et al. (1988)
	Absence vs. presence	Bovey et al. (1987); Baker and Hunt (1988); Peterson et al. (1985); Richard and Slife (1979); Sharma and Vanden Born (1970); Taylor et al. (1981); Veerabhadraiah et al. (1980); Wills (1978)
	Suspected effects	Caseley and Coupland (1980); Whitehouse et al. (1982)
Formulation	Noncommercial	Akey and Morrison (1983); Babiker and Duncan (1975); Baker and Hunt (1988); Baur et al. (1971); Caseley and Coupland (1980); de Ruiter et al. (1988); Devine and Vanden Born (1985); Haderlie (1980); Hamburg and McCall (1988); Hashimoto et al. (1979); Hook and Glenn (1984); Jordan (1977); Kells et al. (1984); King and Radosevich (1979); Kitchen et al. (1980); Muller et al. (1984); Nomura and Hilton (1982); Norris and Freed (1966); Norris (1974); Petersen and Swisher (1985); Reddy and Bendixen (1988); Richard and Slife (1979); Richardson and Grant (1977); Richardson (1979); Richardson (1980); Riederer and Schonherr (1985); Ritter and Coble (1981); Sargent and Blackman (1969); Shafer and Bukovac (1988); Sharma et al. (1978); Shaner and Robson (1985); Todd and Stobbe (1977); Veerabhadraiah et al. (1980); Willingham and Graham (1988); Wills (1978); Wills (1984); Wills and McWhorter (1981); Zabkiewicz et al. (1988)
	Commercial	Bentson (1989); Bovey et al. (1983); Bovey et al. (1987); Eberlein and Behrens (1984); Gillespie and Miller (1983); McCall et al. (1986b); McWhorter and Wills (1978); McWhorter et al. (1980); O'Sullivan and

Table 1. *(Continued)*

Factor or process	Observation	References
Formulation (cont.)		Kossatz (1984); Peterson et al. (1985); Richard and Slife (1979); Richardson (1975); Schultz and Burnside (1980); Sharma and Vanden Born (1970); Taylor et al. (1981); Waldecker and Wyse (1985); Whitehouse et al. (1982)
Quantification	Parent compound	Babiker and Duncan (1975); Baur et al. (1971); Bentson (1989); Bovey et al. (1983); Bovey et al. (1987); Caseley and Coupland (1980); Hashimoto et al. (1979); Hogue (1978); Muller et al. (1984); Nomura and Hilton (1982); Petersen and Swisher (1985); Richardson (1975); Ritter and Coble (1981); Sharma and Vanden Born (1970)
	Radioactivity	Akey and Morrison (1983); Baker and Hunt (1988); Bloomberg and Wax (1978); de Ruiter et al. (1988); Devine and Vanden Born (1985); Eberlein and Behrens (1984); Gillespie and Miller (1983); Haderlie (1980); Hamburg and McCall (1988); Hook and Glenn (1984); Jordan (1977); Kells et al. (1984); King and Radosevich (1979); Kitchen et al. (1980); McCall et al. (1986a); McCall et al. (1986b); McWhorter and Wills (1978); McWhorter et al. (1980); Norris and Freed (1966); Norris (1974); O'Sullivan and Kossatz (1984); Peterson et al. (1985); Reddy and Bendixen (1988); Richard and Slife (1979); Richardson and Grant (1977); Richardson (1979); Richardson (1980); Shafer and Bukovac (1988); Shultz and Burnside (1980); Sharma and Vanden Born (1978); Shaner and Robson (1985); Todd and Stobbe (1977); Veerabhadraiah et al. (1980); Waldecker and Wyse (1985); Whitehouse et al. (1982); Willingham and Graham (1988); Wills (1978); Wills (1984); Wills and McWhorter (1981); Zabkiewicz et al. (1988)
Deposit characteristics	Measured	Baker and Hunt (1988); Bentson (1989); Bovey et al. (1987); Eberlein and Behrens (1984); Taylor et al. (1981); Todd and Stobbe (1977); Whitehouse et al. (1982); Zabkiewicz et al. (1988)

Table 1. *(Continued)*

Factor or process	Observation	References
Plant growth environment	Greenhouse	Akey and Morrison (1983); Babiker and Duncan (1975); Baker and Hunt (1988); Bloomberg and Wax (1978); Bovey et al. (1983); Bovey et al. (1987); Caseley and Coupland (1980); de Ruiter et al. (1988); Devine and Vanden Born (1985); Eberlein and Behrens (1984); Gillespie and Miller (1983); Haderlie (1980); Hamburg and McCall (1988); Hashimoto et al. (1979); Hogue (1978); Hook and Glenn (1984); Jordan (1977); Kells et al. (1984); King and Radosevich (1979); Kitchen et al. (1980); McCall et al. (1986a); McCall et al. (1986b); McCall (1988); McWhorter and Wills (1978); McWhorter et al. (1980); Muller et al. (1984); Nomura and Hilton (1982); Petersen et al. (1985); Peterson et al. (1985); Reddy and Bendixen (1988); Richard and Slife (1979); Richardson and Grant (1977); Richardson (1979); Richardson (1980); Riederer and Schonherr (1985); Ritter and Coble (1981); Sargent and Blackman (1969); Schultz and Burnside (1980); Sharma and Vanden Born (1970); Sharma et al. (1978); Shaner and Robson (1985); Taylor et al. (1981); Todd and Stobbe (1977); Waldecker and Wyse (1985); Whitehouse et al. (1982); Willingham and Graham (1988); Wills (1978); Wills (1984); Wills and McWhorter (1981); Zabkiewicz et al. (1988)
	Field	Bentson (1989); Bovey et al. (1983); Norris and Freed (1966); Norris (1974); Richardson (1975); Shafer and Bukovac (1988); Sharma and Vanden Born (1970)
Concentration	Different levels	Baur et al. (1971); Bovey et al. (1987); Kells et al. (1984); Richardson and Grant (1977); Wills (1984)
Plant moisture status		Akey and Morrison (1983); Kells et al. (1984); McWhorter et al. (1980); Waldecker and Wyse (1985); Willingham and Graham (1988); Wills (1978)

grown seedling may not be representative of the absorption behavior that would occur in the field.

Foliar penetration of a specific substance depends greatly on the plant species. Bentson (1989) shows that foliar penetration of triclopyr herbicide (butoxyethyl ester of [(3,5,6-trichloro-2-pyridinyl)oxy]acetic acid) into giant chinkapin [*Castanopsis chrysophylla* (Dougl.)A. DC.] was greater than into Pacific madrone (*Arbutus menziesii* Pursh.) under identical environmental conditions. Both of these trees grow in similar environments and are evergreen with schlerophillized foliage. Differences in foliar penetration between species using identical treatment solutions and growth environments have been shown by others (Eberlein and Behrens 1984; McWhorter et al. 1980; Sharma and Vanden Born 1970).

2. *Pesticide Formulation*. Pesticides used in penetration studies are frequently not in the form applied in the field. Often the parent acid form of an herbicide is applied rather than the amine or ester forms that are used in the field (Akey and Morrison 1983; Baur et al. 1971; King and Radosevich 1979; Norris 1974; Richardson 1975; Richardson and Grant 1977; Riederer and Schonherr 1985; Sargent and Blackman 1969; Schultz and Burnside 1980; Veerabhadraiah et al. 1980). Some investigators, however, have shown that nonionic forms of pesticides are more readily absorbed by foliage than ionic forms. For instance, Norris and Freed (1966) found that the extent of absorption of 2,4-D ([2,4-dichlorophenoxy]acetic acid) and 2,4,5-T ([2,4,5-trichlorophenoxy]acetic acid) into bigleaf maple (*Acer macrophyllum* Pursh.) depends on the form of the material in the rank ester > acid > amine salt (solution pH unstated).

Lipid solubility of herbicides is an important factor in their ability to penetrate foliage (Baker 1980). Baker and Hunt (1988) investigated the foliar penetration of several compounds with a range in lipophilicity (expressed as the partition coefficient). They found that the greatest foliar penetration occurred with compounds of medium to high lipophilicity. This relation held in the presence of surfactants. Cuticular penetration into yellow foxtail plants [*Seteria glauca* (L.) Beauv.] of six aryloxyphenoxypropionates depends on structural class (pyridinyloxy, quinoxalinyloxy, or phenoxy) rather than on solubility of lipophilicity (Hamburg and McCall 1988). Structural class has a greater effect on cuticular penetration than formulation. The number of compounds in each structural class, however, limits conclusions on solubility and lipophilicity effects of chemicals on cuticular penetration in this study. These studies indicate that the chemical structure and consequent chemical properties play an important role in foliar penetration of pesticides.

Pesticide formulations have a pronounced effect on foliar penetration. The presence of a surfactant has often been demonstrated to enhance foliar penetration by herbicides (Babiker and Duncan 1975; Bovey et al. 1987; Haderlie 1980;

Peterson et al. 1985; Richard and Slife 1979; Sharma and Vanden Born 1970; Taylor et al. 1981; Veerabhadraiah et al. 1980).

The effect of a surfactant is variable. Foliar penetration depends partly on the chemistry of the pesticide, which interacts with the chemical properties of the surfactant and leaf cuticle. Babiker and Duncan (1975) found that the foliar penetration of asulam (methyl sulfanilylcarbamate) into bean (*Vicia faba* var. Maris Bead) is enhanced by nonionic ester and ether surfactants and decreases relative to the pure compound by nonionic alcoholic surfactants; some surfactants that increased penetration did not increase phototoxicity. Penetration of dicamba (3,6-dichloro-*0*-anisic acid) into soybean (*Glycine max* L.) was not increased with nonionic surfactants; penetration did increase with anionic wetting agents plus alkyd stickers and cationic surfactants (Peterson et al. 1985).

Whitehouse et al. (1982) and de Ruiter et al. (1988) demonstrated that some spray formulations and surfactants disrupt the epicuticular wax layer, and both suggested that penetration is a function of both the pesticide compound, formulation components, and plant species. Penetration of NAA [2-(1-naphthyl)acetic acid] into enzymatically isolated cuticles of mature tomato (*Lycopersicon esculentum* Mill. *cv.* Sprinter) fruit showed that below the critical micelle concentration (CMC), surfactants had little effect on sorption (Shafer and Bukovac 1988). Above the CMC, however, sorption decreased with an increase of surfactant concentration. The chemical composition of formulations and plant epicuticular waxes is critical to the diffusion of xenobiotic substances from pesticide deposits.

Few investigators have attempted to characterize properties of the spray solution that are important in spray retention and foliar penetration. Bovey et al. (1987) related absolute surface tension, density, and viscosity to spray retention, and hence the ultimate quantity of herbicide that penetrates target foliage. Eberlein and Behrens (1984) suggest that propanil [*N*-(3,4-dichlorophenyl)propionamide] selectivity for green foxtail [*Setaria viridis* (L.) Beauv.] in wheat (*Triticum aestivum* L. "Era") was due to spray retention. In an analysis of efficacy of bentazon [3-isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one-2,2-dioxide] in control of *Chenopodium album* L., Taylor et al. (1981) showed that the contact angle of the spray mix was important. Whitehouse et al. (1982) suggests that the amount of spreading of the deposit is important in the foliar absorption of pesticides. Zabkiewicz et al. (1988) compared the contact angles, deposit spreading, and drying times of organosilicone and organic surfactants on leaves of bean, eucalyptus (*Eucalyptus botryoides*), and mandarin orange (*Citrus nobilis* var. Ushin, Silverhill strain) plants. Surfactants showed a wide range of interaction with leaf surfaces, spreading more on bean than either eucalyptus or mandarin leaves. Drying times were faster on surfaces where the deposits spread more, and uptake appeared to be less with faster drying. These results contrast with the results of Bentson (1989), where droplet spreading of an aqueous commercial spray formulation of triclopyr and foliar penetration was greater on leaves of giant chinkapin than on those of Pacific madrone. These studies demonstrate the complexity of interactions between droplet spreading and drying and the actual quantity of a substance that penetrates into foliage.

The above studies indicate the importance of using the same chemical forms and spray formulations in studies of foliar penetration as are used in operational applications. This is essential if models of chemical dissipation developed from such studies are to be relevant to field situations. There are also interactions between environmental conditions and the formulation that affect foliar penetration of pesticides.

3. Experimental Environment. The effect of temperature, humidity, photosynthetically active radiation, simulated rainfall, and plant moisture stress on foliar penetration have also been investigated. Gerber et al. (1983) observed that most of the literature focuses on the effect of a single factor and therefore is difficult to use in interpretation of pesticide behavior in the field.

Temperature is pivotal in the physical chemistry of foliar penetration, because of its influence on the chemical potential of a xenobiotic substance, but it has received little attention (Table 1). Most investigators have disregarded temperature or have used only a single temperature regime for absorption experiments in greenhouses and growth chambers.

Gillespie and Miller (1983) found foliar penetration by disclofop (2-[4-(2,4-dichlorophenoxy)phenoxy]propanoic acid) into sunflower (*Helianthus annus* L.) was greater at 30°C than at 10°C. Kells et al. (1984) applied fluazifop-butyl ((±)-butyl 2-[4-[(5-(trifluoromethyl)-2-pyridinyl)oxy]phenoxy]propanoate) to quackgrass [*Agropyron repens* (L.) Beauv.] and soybean, and then placed the plants in growth chambers at either 20° or 30°C. After 144 h, penetration was 45.3 and 71.4% at 20° and 30°C, respectively. McCall (1988) used three temperature levels (13°, 20°, and 30°C) to model the volatilization, penetration, translocation, and metabolism of haloxyfop (2-[4-[(3-chloro-5-(trifluoromethyl)-2-pyridinyl)oxy]phenoxy]propanoic acid) ethoxyethyl and methyl esters on yellow foxtail [*Setaria glauca* (L.) Beauv.]; penetration by haloxyfop increased with increasing temperature. Glyphosate [*N*-(phosphonomethyl)glycine] penetration into hemp dogbane (*Apocynum cannabinum* L.) was found to double when temperature was raised from 25° to 30°C, but this did not occur with 2,4-D (Schultz and Burnside 1980). Amine salts of picloram (4-amino-3,5,6-trichloropicolinic acid) and 2,4-D were applied to field-grown quaking aspen (*Populus tremuloides* Michx.) and balsam poplar (*Populus balsamifera* L.), which were then placed in chambers at either 10°, 25.5°, or 40.5°C. With this technique, Sharma and Vanden Born (1970) found that penetration increased with increasing temperature. Bentson (1989) showed that trichlopyr penetration into giant chinkapin increased with higher temperatures (10°, 25°, and 40°C); however, penetration into Pacific madrone increased only between 10° and 25°C and not between 25° and 40°C.

In most instances, higher temperatures increase foliar penetration. The possibility of decreased foliar penetration by a substance at higher temperatures could also occur. For instance, McWhorter et al. (1980) found that glyphosate penetration into soybean is higher at 24°C than at 29.5° and 35°C. They also found that penetration of glyphosate into Johnsongrass [*Sorghum halepense* (L.) Pers.] increases with higher temperatures under the same experimental conditions. This suggests that with certain compounds in specific formulations on certain plant species foliar penetration does not necessarily increase with increasing temperatures. Studies not using different temperatures will produce information of limited use for characterizing the field behavior and environmental fate of pesticides in foliar deposits.

Humidity also influences foliar penetration, but it has been investigated to an even lesser extent than temperature (Table 1). The foliar penetration studies that investigated humidity mostly did so with acidic, basic, or polar herbicides.

Babiker and Duncan (1975) used a low humidity level (bean plants in chamber) versus a high humidity level (bean plants in plastic bags in chamber) and found that asulam without surfactant had five to six times less penetration under low humidity than under high humidity. Addition of surfactant offset this difference only partially; asulam penetrated about three and a half to four times less at low humidity than at high humidity. Glyphosate penetration into bermudagrass at 40% relative humidity (RH) and 22°C was less than 10% of the applied quantity; while at 100% RH and 32°C penetration was greater than 70% (Jordan 1977). Sharma and Vanden Born (1970) did not measure humidity, but in their study of penetration of picloram and 2,4-D amine salts into quaking aspen and balsam poplar, high humidity doubled the amount of both herbicides penetrating the foliage when compared with results from low-humidity treatments at the same temperature. Taylor et al. (1981) measured efficacy of bentazon in *Chenopodium album* L., and found that 40% RH nearly doubled efficacy when compared to plants treated under a 80% RH regime. Wills and McWhorter (1981) found that acifluorfen (5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid) penetration into soybeans [*Glycine max* (L.) Merr. "Lee 68"], was four times greater at 100% RH than at 40%, regardless of temperature. Similarly, Wills (1984) found that absorption of sethoxydim (2-[1-(ethoxyimino)-butyl]-5-[2-(ethylthio)-propyl]-3-hydroxy-2-cyclohexen-1-one) by bermudagrass increased at higher RH levels. The information on humidity is limited, and it is difficult to draw substantive conclusions, although it appears that high humidity may facilitate penetration of some acidic, basic, and polar substances into foliage. Humidity in conjunction with plant moisture stress affects stomatal aperature, which is a route of foliar penetration in some instances. The thickness and composition of epicuticular wax layers depends to some degree on the average humidity during leaf development (Baker 1980). Thus the effect of humidity on the plant both physiologically and developmentally may affect foliar penetration.

Willingham and Graham (1988) investigated the effects of relative humidity, temperature, and soil moisture on the foliar penetration of acifluorfen into velvetleaf (*Abutilon theophrasti*). Relative humidity correlated with the greatest foliar penetration, which had been observed in the field and laboratory (Ritter and Coble 1981; Wills and McWhorter 1981). Temperature had the second largest effect on penetration. Soil moisture was observed to significantly affect foliar penetration. This study indicates that under field conditions, foliar penetration would be a complex function of all these factor's environmental levels.

Plant moisture stress has been investigated to a limited extent (Table 1). Akey and Morrison (1983), investigating diclofop penetration into wild oats using two different soil moisture contents (10 and 20% w/w), showed that penetration was initially slower at the lower soil moisture content, but that 48 h after application there was no difference in the quantity that had penetrated into foliage. Penetration of fluazifop-butyl into quackgrass and soybean showed no difference in penetration when plants were stressed at 6–10% (w/w) soil moisture content or at field capacity (21%); however, quackgrass showed greater mortality with herbicide treatment when moisture stressed (Kells et al. 1984). Glyphosate treatment of common milkweed (*Asclepias syriaca* L.) had 44% versus 29% of the applied quantity absorbed by plants at 25% and 13% (w/w) soil moisture content, respectively (Waldecker and Wyse 1985). The total time between application and recovery was not given for this study, however. McWhorter et al. (1980) showed that glyphosate penetration into Johnsongrass was greater at 20% soil moisture (w/w) than at 12%.

Plant moisture stress, and soil moisture content, seem to have some effect on the rate of penetration but may not be important in determining the ultimate amount of a pesticide that penetrates foliage. Davies et al. (1983) has suggested that soil moisture effects on stomata could be used to increase the efficacy of some herbicide treatments by increasing the stomatal pathway of foliar penetration through maintenance of high soil moisture content to ensure the stomata are open.

Bovey et al. (1983) applied triclopyr to honey mesquite [*Prosopis juliflora* var. *glandulosa* (Torr.) Cockerell] in both the laboratory and the field. They noted that the amount of triclopyr acid in tissues increases with time from ester degradation and that 24 h after a field spray application, no triclopyr remains in foliar surface deposits. Simulated rainfall was used to determine if rain soon after application would decrease the absorption of triclopyr. They found that triclopyr penetration into foliage was unaffected by rain. Caseley and Coupland (1980) also used simulated rain to determine the effect on absorption of difenzoquat (1,2-dimethyl-3,5-diphenyl-1*H*-pyrazolium methyl sulfate) in wild oat and found that absorption was reduced by rainfall that occurred within a hour of application; this reduction was not as evident if rain occurred 4 h after application. There is little other information in the literature on the effect of rainfall on foliar penetration, although rainfall does have the potential for decreasing the level of a material that enters foliar tissues.

4. Time Course. Most investigators of the absorption of pesticides by foliage look at the change in quantity of a substance in leaf tissues at several different times afater application (Table 1). Many of the studies do not track foliar penetration until it approaches a steady state quantity in the tissues. The steady state concentration is actually a more important value in determining the quantity of pesticide that is absorbed than the rate a pesticide penetrates foliage, because it defines the maximum attainable quantity of a pesticide in tissues from a deposit under specified environmental conditions.

In general, most sampling times are chosen as a series, in a pattern like 2, 4, 8, 16, and 32 h, chosen on the rationale that they will better characterize the exponential nature of foliar absorption (Akey and Morrison 1983; Babiker and Duncan 1975; Bloomberg and Wax 1978; Bovey et al. 1983; Devine and Vanden Born 1985; Eberlein and Behrens 1984; Gillespie and Miller 1983; Haderlie 1980; Hamburg and McCall 1988; Hashimoto et al. 1979; Hook and Glenn 1984; Kells et al. 1984; Kitchen et al. 1980; McCall 1988; McCall et al. 1986a; Muller et al. 1984; Nomura and Hilton 1982; O'Sullivan and Kossatz 1984; Petersen and Swisher 1985; Richard and Slife 1979; Richardson 1975; Richardson 1979; Richardson 1980; Ritter and Coble 1981; Schultz and Burnside 1980; Sharma and Vanden Born 1970; Todd and Stobbe 1977). To avoid the assumption that the rate of foliar penetration is exponential, evenly spaced time intervals have been used (Bentson 1989). Others have looked at one or two different times, with no reference as to whether they reached the time of steady state maximum absorption (Baur et al. 1971; Casely and Coupland 1980; Hogue 1978; King and Radosevich 1979; Norris and Freed 1966; Peterson et al. 1985; Richardson and Grant 1977; Shaner and Robson 1985; Veerabhadraiah et al. 1980; Waldecker and Wyse 1985). The distribution over time of a pesticide into tissues is critical for the evaluation of environmental fate. In the field, other dissipative and degradative processes will be occurring simultaneously with foliar penetration and will thus alter the rate and quantity of a material entering tissues.

5. Environmental Fate. Few investigators have considered if other dissipative or degradative processes are occurring during the foliar absorption experiments (Table 1). Dissipative and degradative processes can alter the rate and final quantity of a pesticide entering leaf tissues by changing the concentration gradient between the deposit and tissues (Nobel 1983).

McCall et al. (1986a) and McCall (1988) used a microagroecosystem to explore foliar penetration and metabolism of tridiphane [2-(2,2,2-trichloroethyl)-2-(3,5-dichlorophenyl)oxirane) and haloxyfop, respectively, on foxtail species (*Setaria* spp.). The approach was to simultaneously measure the rates of volatilization, foliar penetration, metabolism, and translocation of the herbicides. Bentson (1989) observed the effect of ultraviolet light and darkness on the foliar penetration and loss of triclopyr in deposits on Pacific madrone and giant chinkapin leaves at 10°, 25°, and 40°C. Although light significantly increased losses of triclopyr from surface deposits versus losses in the dark, foliar penetration was not significantly different, except at 25°C with giant chinkapin leaves. These approaches monitor the effects of simultaneous dissipative and degradative phenomena to develop models for predicting field behavior of the herbicides.

6. Chemical Analysis. Most studies that have investigated foliar absorption of pesticides detect only radioactivity (Table 1). The fate of the actual parent compound in the tissues is unknown. The physical chemistry of chemical penetration into foliar tissues is highly dependent, however, on the concentration of the parent pesticide, in both deposits and tissues. The actual concentration of the parent compound in tissues is usually unknown when radiotracers are used. Results are reported as the percentage of applied radioactivity, and radioactive metabolites may be confused with the original substance. This lack of definitive information is a weakness that makes most of the data generated from foliar penetration studies using radiolabeled chemicals poor for environmental fate interpretation and modeling.

McCall et al. (1986a), McCall et al. (1986b), McCall (1988) and Hamburg and McCall (1988) have used radiolabeled materials and high-pressure liquid chromatography with radiometric detection to isolate active ingredients from metabolites. This approach removes the uncertainty of whether the radiation detected is the active ingredient or metabolites. Another approach is to use classical residue analyses to determine the quantity of active ingredient in different compartments.

B. Mechanistic Foliar Penetration Studies

A few studies have investigated the diffusion of herbicides across isolated cuticles, or for effects of cuticular structure and composition, and surface morphological characteristics of leaves on foliar penetration (King and Radosevich 1979; Norris 1974; Riederer and Schonherr 1985; Shafer and Bukovac 1988; Taylor et al. 1981; Whitehouse et al. 1982).

Chamel (1986) provides a review and other references in this area. Studies using isolated cuticles generally are attempting to define the Fick's first law diffusion coefficient by various properties of the cuticle. The studies often separate the effects on diffusion of epicuticular wax composition versus the thickness of the cuticular layer under the epicuticular waxes (Riederer and Schonherr 1985; Taylor et al. 1981; Whitehouse et al. 1982). Baker (1980) reviewed the literature of foliar penetration by herbicides for the chemical composition of cuticles, but this approach has provided mixed results. The assumption that the cuticle composition and structure defines the quantity of pesticide entering leaf tissues is not completely correct, because the chemical potentials of a substance within the deposit, cuticle, atmosphere, and tissue compartments defines the amount of penetration that will occur. Other studies (King and Radosevich 1979) show the effect of differential absorption into morphologically distinct structures in cuticles such as stellate trichomes, adaxial versus abaxial leaf surfaces, and stomata. Davies et al. (1983) reviewed the literature for the manipulation of stomatal behavior to improve herbicide foliar penetration.

Mechanistic foliar penetration studies uniformly ignore the influence of environment and are subject to many of the same limitations as empirical foliar penetration studies for the determination of environmental fate.

III. Volatilization

Compared to foliar penetration of pesticides, far less research has focused on the volatilization of pesticides from deposits on foliage. Baskin and Walker (1953) were the first to unequivocally demonstrate that vapors of 2,4-D and 2,4,5-T formulations are toxic to plants (tomatoes). Most of the literature is on volatilization of materials from water or soil, environmental compartments that are dissimilar to foliar surfaces. Spencer et al. (1973), in a review of volatilization, noted that there is virtually no information on volatilization from foliar surfaces; this is still true. Jury et al. (1987), for example, in a review of the fate of organic chemicals in the soil–air–water ecosystem, ignore the issue of residues on foliage, although plants are a key component of ecosystems and commonly have pesticides applied to them.

A. Physical Chemistry

Several excellent treatments of the physical chemistry of volatilization are available (Hartley and Graham-Bryce 1980; Mackay 1985; Plimmer 1976; Spencer et al. 1973; Taylor and Glotfelty 1988; Thibodeaux and Scott 1985), and the reader is referred to these for detailed descriptions. One limitation in most of these treatments is that they ignore volatilization from formulations and from deposits on foliage.

Volatilization is, in the strict sense, the escape of vapor of a pure compound into the gas phase from a liquid or solid condensed phase of the pure substance. Thus vapor pressure is a key descriptor in quantifying volatilization. This differs markedly from situations in the field where a pesticide is not in its pure condensed phase, but is dispersed over a large area and associates with a variety of materials (e.g., water, soil constituents, epicuticular waxes of foliage, and formulation components). As Hartley (1983) indicates, bioassay measurements of "volatilization" are a misnomer, because there is also the component of uptake of vapor by indicator species.

The vapor pressure of a substance is a function of temperature. Under field situations, temperature is important in the volatilization of a pesticide, but wind, Raoult's and Henry's laws, diffusion in air, and humidity are also key determinants, which to a greater or lesser extent also depend on temperature. Wind controls the thickness of stagnant air boundary layers over surfaces a substance must diffuse through and is important in the advection of substances away from a site.

There are practical limitations in using the physical chemical properties of a substance to describe volatilization from a foliar deposit. Use of the Henry's law constant is well developed for volatilization of materials from water (Suntio et al. 1988), but the Henry's law constants for pesticides in formulations are unknown because (1) the solubility of a pesticide in a formulation is unknown, (2) the vapor pressure for the form (e.g., amine salt, ester) of a pesticide is also seldom known, although it can be approximated (Lyman 1985), (3) the effect on the Raoult's or Henry's laws constants of partial mixing of epicuticular waxes with the formulation in a deposit has not been assessed, and (4) the effect of dissipation of other formulation components has not been measured.

The complexity of leaf shapes and orientation make estimating the boundary layer thickness directly over a deposit difficult (Hartley and Graham-Bryce 1980). The boundary layer partially controls the diffusion of a substance from a deposit into the air, and diffusion coefficients for the forms of a pesticide in air are rarely known. The effect of humidity on the composition of deposits is also unknown. Some deposits are hygroscopic, but some deposit constituents are hydrophobic. Dew on surfaces with pesticide deposits increases loss of some pesticides from surface deposits (Willis et al. 1980). Modification of volatilization of pesticides by competing processes such as foliar absorption and photodegradation, has rarely been evaluated.

Some studies have determined the volatilization of pesticides from formulations. Holoman and Seymour (1983) used glass surfaces as substrates to measure volatile losses of pesticides from formulations. With this technique, they evaluated volatilization loss of chlorpyrifos [*O,O*-diethyl-*O*-(3,5,6-trichloro-2-pyridyl)phosphoro-thioate] from Lorsban 4E emulsion sprays applied to petri dishes and compared the effects of hollow-cone versus flat-fan spray nozzles, different added adjuvants to the emulsion, and the differences between different lots of the formulation. Deposits from flat-fan nozzles had less volatilization, as did deposits with adjuvants versus the commercial formulation alone. Interestingly, slight differences in volatility of chlorpyrifos from different pesticide lots were also shown.

Sundaram (1985) used a gravimetric technique to show that different formulations and additives have different rates of volatilization. The relation between formulation composition, component volatility, and environmental conditions needs further investigation to improve spray deposition and efficacy and to minimize environmental contamination (Hartley 1983). The effects that foliage contributes to these phenomena have not been explored.

B. Field Studies

Seiber and Woodrow (1983) provide an overview and further references on sampling techniques for volatilized residues from sprayed sites. The general sampling technique is to place suitable sampling devices in a recently sprayed field, and capture residues out of a known volume of air. These measurements are sometimes made alone, or with concurrent samples of foliage and soils. Sampler intake is either at one or several heights to sample within the crop canopy and the boundary layer above the canopy.

Seiber et al. (1979) investigated toxaphene (a mixture of polychlorinated bicyclic terpenes) volatilization from treated cotton (*Gossypium hirsutum* L.) including foliar and soil samples. Volatile toxaphene fractions (commercial formulations contain up to 177 different compounds that are the active ingredients) were lost more rapidly than less volatile fractions, showing a rapid increase in air samplers after application and a rapid decrease in foliar quantities. Seiber et al. (1979) noted that differences in dissipation rates between their study and others were probably due to formulation, application rate, foliage texture, and meteorological conditions. Harper et al. (1983) investigated toxaphene and DDT ([1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane]) volatilization from cotton, and found that the foliar canopy was the major source of volatilized residues and the observed flux of materials was directly related to the quantity of pesticides on foliage. Volatilization was also correlated with air temperature and net radiation (insolative heat load). A comparison of microencapsulated and emulsifiable concentrate formulations of methyl parathion (*O,O*-diethyl-*O*-*p*-nitrophenyl phosphorothioate) showed that its volatilization was greater from emulsifiable concentrate formulations (Jackson and Lewis 1979). This evidence suggests that the volatilization of pesticides is closely related to the amounts of pesticides on foliage, meteorological conditions, and formulation.

Grover et al. (1972) investigated vapor drift of the butyl ester and dimethylamine formulations of 2,4-D and 2,4,5-T for a half-hour post-application. About 25–30% of the butyl ester formulations volatilized, but only 3–4% of the dimethylamine formulations did so. This study shows a weakness common in volatilization studies, in that the vegetation (composition, leaf area index, and stature), and proportion of exposed soil were not reported, thereby making the deposit site contributing the volatilized residues difficult to determine.

Taylor et al. (1977) and Taylor (1978) discuss the volatilization of two insecticides, dieldrin (1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4*a*,5,6,7,8,8*a*-octahydro-endo-exo-1,4:5,8-dimethanonaphthalene) and heptachlor (1,4,5,6,7,8,8-heptachloro-3*a*,4,7,7*a*-tetrahydro-4,7-methanoindene), from vegetation. They report that in 30 d about 90% of dieldrin residues had volatilized, based on multipoint air sampling. They concluded that volatilization was the major dissipative process causing the observed losses of the residues from leaf surfaces; however, other studies have shown photodegradation of dieldrin to be significant (Robinson et al. 1966; Zabik et al. 1976). Measurements by Taylor et al. (1977) and Taylor (1978) of volatilized residues were done only for the first 14 h after application. Based on these results, volatilization is the primary loss process in the initial half-day after application.

Field studies not observing levels of residues in other compartments besides the atmosphere are not useful for modeling the environmental fate of pesticides. The source concentration and chemical environment of a residue in or on compartments has a strong influence on residue volatilization. Most field studies do not gather detailed meteorological information, which limits the usefulness of the data for exposure assessments and environmental fate modeling. A weakness of field studies is that the proportion of the actual flux sampled is not known. Thus, there is great uncertainty as to the representativeness of point sample measurements.

C. Microcosm and Greenhouse Studies

Microcosm and greenhouse studies can overcome many of the problems with limited data that are present in field studies, because all the volatilized residues can be captured, and meteorological conditions and application parameters can be closely controlled. Microcosm (or microagroecosystem) studies in particular can control and monitor parameters (Nash 1983), thus providing data useful for environmental fate modeling.

Boldt and Putnam (1980) in a study of selectivity mechanisms of diclofop methyl including foliar penetration and volatilization in the greenhouse with uncontrolled temperatures, found that losses from foliar surfaces and glass cover slips were about equal (by mass balance).

Microcosm studies have been more precise. Nash et al. (1977) used a microagroecosystem to study volatile losses of toxaphene and DDT from leaf surfaces and glass slides. Temperatures in these experiments were uncontrolled, but quantities of the residues in foliage, soil, and on glass slides were determined. Differences in quantities volatilized from soil versus foliage could not be determined, because the site of spray deposition was uncontrolled. Separation of volatilization from soils and foliage would improve understanding of the source of volatilized residues.

McCall et al. (1986a) used radiolabelled tridiphane, controlled temperatures, and foliar applications (none to soil) in a microcosm. Glass slides were used to establish the volatilization rate from the formulation without the influence of foliage. Using this technique, they were able to show the influence of parameters such as drop size, the addition of atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine], and temperature on the subsequent environmental fate of tridiphane. Higher temperatures caused an increase in the rate of volatilization. An outdoor application was used to provide field data to test the models. McCall (1988) used a similar approach to evaluate the short-term environmental fate of haloxyfop.

Microcosm studies are valuable tools for developing models of the fate of pesticides in foliar deposits, as shown by McCall et al. (1986b) and McCall (1988). The correct selection of parameters is necessary to fully evaluate the fate. For instance, no microcosm study has evaluated the effect of humidity or sunlight (particularly UV radiation) on the subsequent fate of pesticides in foliar deposits, although these are common conditions in the field.

IV. Photodegradation

Several pesticide photodegradation investigations and extensive reviews (Choudry and Webster 1985; Crosby 1976; Marcheterre et al. 1988; Zabik and Leavitt 1976). This review cannot discuss specific reaction mechanisms, but will discuss the research approaches used to investigate pesticide photodegradation and the limited literature that exists on the photodegradation of xenobiotic substances in foliar pesticide deposits.

A. Laboratory Investigations of Photodegradation

Most mechanistic studies of pesticide photochemistry have been either in organic solvent or aqueous systems (Marcheterre et al. 1988). Concentrations of pesticides are often greater than would occur in water under field situations. The radiation used for the investigations is not very similar to sunlight, because it is a narrow band centered either around 308 nm, produced by low-pressure mercury vapor lamps, which is in the solar spectrum reaching the Earth's surface, or 254 nm, generated by high-pressure mercury lamps, which is not present in insolation at the Earth's surface (Crosby 1976). Photochemical reactions are usually observed under artificial conditions with controlled temperature and solution composition. These conditions are consistent with study goals, which generally are to understand the different photoproducts and degradation pathways.

As has been mentioned previously, surfactants are important components in foliar pesticide deposits. Tanaka et al. (1979) studied the effects of surfactants on the degradation of several herbicides. They believed that monuron [3-(*p*-chlorophenyl)-1,1-dimethylurea] photodegradation was occurring in the organic phase of surfactant micelles, based on the lack of products that showed oxygen involvement. It was concluded in another paper (Tanaka et al. 1981) that surfactants increase the photodegradation rates of herbicides having (1) low water solubilities, (2) chloro substitutents on aromatic rings, or (3) triplet energies below those of the surfactant. Surfactants in foliar pesticide deposits may play a role in the photodegradation of xenobiotic substances, either as sensitizers or as proton donors.

There are several limitations to much of the photodegradation research on pesticide environmental fate. It is questionable whether photodegradative pathways and rates observed in solvents, such as methanol, acetonitrile, or acetone, are the actual pathways and rates that would occur under field conditions in water or foliar pesticide deposits. Photochemical mechanisms are known to vary with changes in the concentration of a substance in solution (Crosby 1976), which means that studies not observing photodegradation in solutions with concentrations similar to those in the field may be misleading. The effect of temperature is frequently ignored, although some actinometer systems are temperature sensitive (Crosby 1976). Therefore temperature should be considered in photodegradation studies to represent the situation in the field. The radiation used for photolysis is either in a band not present in sunlight or is a narrow portion of the solar spectrum at the Earth's surface. Photolysis mechanisms and rates therefore are not representative of those occurring under field conditions. These factors make extrapolation of laboratory photolysis data to field situations difficult and prone to error (Miller and Zepp 1983).

The quantitative and theoretical aspects of photodegradation in aqueous systems is very well developed (Choudry and Webster 1985; Mill and Mabey 1985; Miller and Zepp 1983). The photochemistry of xenobiotic substances in foliar deposits, where there are high concentrations of several substances potentially involved in photolysis, is relatively undeveloped. There is increasing interest in vapor phase photolysis (Woodrow et al. 1983). Pesticide vapor is produced under controlled laboratory conditions and illuminated with ultraviolet radiation for a specific time; the photoproducts are subsequently assayed.

B. Photodegradation on Foliage in Field and Microcosm Studies

Most studies of photodegradation on foliage have been performed in outdoor studies. Microcosm studies generally have not considered photodegradation in experimental protocols (McCall 1988; McCall et al. 1986a; McCall et al. 1986b; Nash 1983). Photodegradation in field situations, however, could have substantial effects on the partitioning of organic substances in the environment. Many outdoor studies of photodegradation have not considered the effect of volatilization and other degradative paths on the parent compound or photodegradation products.

Makary et al. (1981), investigating the photolysis of phoxim (4-ethoxy-7-phenyl-3,5-dioxa-6-aza-4-phosphaoct-6-ene-8-nitrile 4-sulfide), used thin-layer chromatography to identify the parent compound and other degradation products. They found that the photoproducts associated with tomato leaves were present in both surface leaf rinses and tissues, and noted that a product of thermal degradation was present. This shows that foliar penetration of reaction products can occur and may need to be measured. Makary et al. (1981) did not present data on insolation, however, or the losses that may have occurred from volatilization. Matsuo and Casida (1970) investigated the photodegradation of radiolabelled dinobuton [1-methylethyl 2-(1-methylpropyl)-4,6-dinitrophenyl ester of carbonic acid] and dinoseb [2-(1-methylpropyl)-4,6-dinitrophenol] on bean leaves in sunlight. They found that different photoproducts form rapidly with exposure to sunlight and that both the photoproducts and parent compounds are lost over time, presumably by volatilization.

Takahashi et al. (1985) showed that, unlike in water, sunlight photodegradation of the pyrethroid insecticide fenpropathrin [2,2,3,3-tetramethylcyclopropanecarboxylic acid cyano(3-phenoxyphenyl)methyl ester] on mandarin orange leaves in a noncommercial formulation does not occur. They concluded that fenpropathrin is lost primarily via volatilization or metabolism in the plant tissues, because few of the photodegradation products could be recovered in either surface washes or tissue extracts. Neither volatilization of photoproducts, a potential path of loss, nor insolation were measured.

Joiner and Baetcke (1973) found parathion photodegradation products in cotton foliage exposed to light in growth chamber, open field, and greenhouse environments. They concluded from mass balance calculations that photodegradation is the sole process in the disappearance of parathion. The analytical procedure, however, did not discern between residues in versus on foliage. El-Sebae et al. (1982) determined that thanite (isobornyl thiocyanoacetate, technical) on cotton plants is degraded primarily by ultraviolet light (60% in 14 h) and found a similar loss in sunlight. Degradation products were not identified, and surface deposits were not separated from leaf tissues. Glass petri dishes were used to evaluate photodegradation in the absence of metabolism. No attempt was made to determine if the observed losses were the result of some other dissipative or degradative process.

The above two studies measure loss of a pesticide in sunlight, but they do not separate residues in tissues from those remaining in deposits. This is a weakness, in that residues in tissues are not likely to photodegrade if ultraviolet radiation is required, because the epicuticular waxes and intervening tissues form a radiation barrier. Another consideration is that losses of these materials could also be from either degradation within plant tissues or volatilization. The above studies did not determine whether the observed phenomena occurred in the absence of radiation.

Slade (1966) applied droplets of a noncommercial formulation of paraquat (1,1′-dimethyl-4,4′-bipyridinium ion) to tomato and bean plants, and tracked the change in residue quantity over time. Quantities in tissues and deposits were not separated. When plants were kept in the dark for 24 h after paraquat application, to allow penetration before exposure to sunlight, and then placed in sunlight, 84% of the applied paraquat was recovered, versus a 58% recovery when the plants were immediately exposed to sunlight after application. Crosby and Wong (1977) applied TCDD (2,3,7,8-tetrachlorodibenzo-*p*-dioxin) in a 2,4,5-T herbicide formulation to rubber plant (*Ficus elastica*) leaves and subsequently exposed some leaves to a day of sunlight while another set was maintained in the dark. They showed that TCDD rapidly degraded in sunlight but not in the dark. They concluded that loss of the residue is the result of exposure to sunlight and, presumably, photodegradation.

A factorial study of triclopyr foliar penetration and dissipation from deposits on giant chinkapin and Pacific madrone foliage used dark and light (UV spectra similar to the sun's) treatments to assay the effect of photodegradation (Bentson 1989). Loss of triclopyr in the light depended on the rate of foliar penetration. For instance, loss of triclopyr in the light at 10°C, at which penetration was negligible, from giant chinkapin leaves was nearly 10 times greater than losses in the dark. At 40°C, however, where triclopyr penetration into chinkapin foliage was large, there was no significant difference in triclopyr loss. Foliar penetration of triclopyr into chinkapin leaves at 25°C was significantly reduced in the light versus the dark treatments. This study demonstrates the interaction among foliar penetration, loss of a substance in light, and environmental conditions on the fate of a substance. Fate studies of photolabile chemicals in pesticide deposits on foliage should assay volatilization, photodegradation products, and foliar penetration to accurately depict the interaction of these processes in the field.

The amount of ultraviolet insolation is important in modeling the fate of xenobiotic substances in the environment. It is frequently measured in outdoor studies of the photolysis of substances in water, but rarely in photolysis studies using foliage. Some studies have measured photolysis in the absence of formulation components, which Tanaka et al. (1979, 1981) showed to be important in some instances. Frequently, dark controls are not maintained at the same temperatures as the outdoor exposed materials, which means that although photodegradation is the likely candidate for the observed photoproducts, other degradative and dissipative processes may have been the cause of the observed losses. Volatilization was suggested as an important path of loss for some residues in several of the papers, as was foliar penetration. The studies, however, provide no way to assess the relative importance of these other disappearance paths. For environmental fate models and exposure assessments, detailed information about the interactions of disappearance phenomena are required, along with monitoring of insolation and meteorological conditions.

V. Discussion and Synthesis

The major dispositional processes for most pesticides and xenobiotic substances in pesticide deposits on foliage have been discussed in the previous three sections. Although many authors studying the persistence of pesticides in or on foliage suggest that one or more of these phenomena are operating, few studies have focused on the interaction of processes or on their effect on the quantities of residues in different compartments. In this section, a conceptual model based on chemical potential is developed to provide insights on some phenomena and the interactions between processes. Although chemical potential is for solution phase systems, it provides a conceptual framework for illustrating the importance of considering different temperatures, humidities, plant species, and deposit and leaf surface compositions in studies of the fate of substances in pesticide deposits on foliage. The collection of suitable data for modeling the fate of substances initially in pesticide deposits is discussed.

This section will address the following questions.

1. What are important physical characteristics of the leaf–deposit–air system?
2. What are the effects of various environmental conditions on dispositional processes?
3. How do processes interact to cause the observed environmental disposition of a substance?
4. What is an efficient study design for evaluating the effects and interactions of environmental conditions on the disposition of substances in pesticide deposits on foliage?

A. Compartments of Leaf–Deposit–Air System

There are three distinct components to the system, each having unique physical and chemical characteristics. The system is divided by two interfaces: one between the leaf tissue and deposit compartments, and other between the deposit and atmosphere.

The leaf tissue compartment is a complex chemical system with hydrophilic and hydrophobic regions, that can also be thought of as barriers to the free diffusion of hydrophobic or hydrophilic substances. Some portions of the tissue are solids, while other parts are primarily liquid.

To simplify the system for this discussion, the discussion will take a macroscopic view and assume that (1) leaf tissues are gelatinous, (2) surfaces are homogeneous on the scale of the deposit areas (ignoring microscopic irregularities), (3) physiological processes are relatively stable in the short term, (4) the tissues are compartmented with limited diffusion between compartments in the short term, and (5) metabolism is minimal in the short term. The epicuticular waxes are the physical interface between the tissues and the deposit, and the assumption is made that the epicuticular wax layer volume is insignificant to the volumes of the deposit and the leaf tissue.

The leaf tissue volume that an herbicide may eventually enter is unknown and difficult to measure. This volume is probably finite, but the fraction of foliar tissue that a substance may penetrate into within this volume is usually unknown. For instance, lipophilic substances would tend to concentrate in tissue locations that had little water and were nonionic, such as membranes.

The deposit is initially a liquid that turns into a semisolid liquid (sometimes with crystallization of components) as the carrier evaporates (Hartley and Graham-Bryce 1980). The deposit is a complex mixture of surfactants, solvents, adjuvants, and clays (sometimes) and usually contains a high concentration of a pesticidal substance. The deposit is bound on one side by the leaf tissues and on the other side by the atmosphere. Diffusion can be in both directions from the deposit.

The atmosphere has an infinite volume. The atmosphere beyond the umixed layer above the deposit is always infinitely dilute in the concentration of a substance.

1. Interfaces. The leaf surface, deposit, and atmosphere interact through their surface tensions to determine the contact angle and degree of spreading of a deposit droplet (Hartley and Graham-Bryce 1980). The mathematical relationship that expresses this is $\cos \theta = (\gamma_{LA} - \gamma_{LD})/\gamma_{DA}$, where θ is the contact angle between the plane of the leaf surface and the upper surface of the deposit droplet, γ_{LA} is the surface tension between the leaf and the atmosphere, γ_{LD} is the surface tension between the leaf surface and the liquid deposit, and γ_{DA} is the surface tension between the deposit and the atmosphere. A contact angle of less than 90° indicates that a droplet wets the surface. The leaf surface area that a droplet contacts increases with a decrease in the contact angle.

A low contact angle means the surface tension between the deposit and surface is low. A low surface tension is the result of the affinity of the deposit solution to the surface coating. This affinity and wetting propensity also means that the surface coating may be miscible in the deposit constituents and vice versa. Whitehouse et al. (1985) showed this in their study, where epicuticular waxes were disrupted more by a formulation with a lower contact angle than with a greater contact angle.

The epicuticular wax layer could be considered a separate compartment with its own volume. It should be remembered in the development of recovery procedures for residues in surface deposits on foliage that epicuticular waxes represent a morphologically distinct layer. Solvents will remove this layer to a variable extent. This can make a large difference in measurements of the quantity of a substance that remains on leaf surfaces if the amount of the substance in the wax layer is large relative to that actually in subcuticular tissues, and various solvents remove different amounts of the wax layer.

Diffusion across the leaf–deposit interface will follow Fick's first law of diffusion on a macroscopic scale. Microscopic features may be involved in differences observed among species or within a species' foliage. The apparent diffusion will occur as if the barrier is uniform and the diffusion rate is equal to the diffusion across the least permeable layer.

Loss of material from a deposit by volatilization involves the leaf–atmosphere interface. This follows Fick's first law of diffusion because of the unmixed boundary layer of air near the leaf surface. The thickness of this boundary layer depends on the air speed above the deposit, which in turn determines the concentration gradient (Hartley and Graham-Bryce 1980; Nobel 1983). A material leaves the deposit, however, also according to either Henry's or Raoult's laws. Actual diffusion may appear to be intermediate between Henry's and Raoult's laws, depending on the properties of the solute and solvent. Both laws are special cases of chemical potential.

B. A Conceptual View of Substance Dynamics in Foliar Deposits

The concept of chemical potential was developed for solutions. Pesticide deposits are either very viscous or solid solutions. Chemical potential, although not directly applicable to the situation of pesticide deposits on foliage, does provide a useful conceptual framework. The following simple discussion is provided for readers who may not be familiar with certain aspects of chemical potential. Those familiar with chemical potential may wish to proceed to following sections.

The chemical potential for a substance j in solution is defined by $\mu_j = \mu_j^* + RT \ln a_j + z_jFE$. The terms are μ_j is the chemical potential of substance j, μ_j^* is the standard-state chemical potential for substance j in the solution, R is the molar gas constant, T is the temperature (° Kelvin), a_j is the activity of the substance j in the solution and it is equal to $\gamma_j X_j$ (X represents the mole fraction, γ is the activity coefficient), z_j is the charge number, F is a Faraday, and E is the electrical potential in volts. The above equation is for ionic substances; the equation for nonionic substances is the same but without the z_jFE term. We have not included gravitational and hydrostatic pressure terms because they are insignificant contributors to the chemical potential in the situation we are discussing. The activity coefficient indicates the deviation of the system from ideality, and can be either positive or negative. Freed and Witt (1969) indicate that chemical potential is a useful concept for the development of herbicide formulations to enhance foliar penetration.

A substance moves from an area of higher chemical potential to an area of lower chemical potential and continues to do so until the chemical potential is equal in each compartment. Fick's first law of diffusion is a special case of the chemical potential of a substance, since for a nonionic substance the flux J_j across some distance x is expressed by the equation, $J_j = -\mathrm{u}_j RT\, \partial \gamma_j c_j / (\gamma_j\, \partial x) = -\mathrm{u}_j RT (\partial c_j)/(\partial x)$ where u_j and c_j are the mobility and concentration of species j, respectively. Fick's first law is expressed by the equation, $J_j = -D_j\,(\partial c_j / \partial x)$, the Fick's first law diffusion coefficient (D_j) is therefore equal to the term $\mathrm{u}_j RT$, and is dependent on temperature (Nobel 1983).

Henry's law is also a special case of the chemical potential. Because the Henry's law constant is a proportionality between a substances partial pressure to its solubility, then this is an expression that its chemical potential as a gas is equal to its chemical potential as a solute at equilibrium. Raoult's law can similarly be derived. The above two analyses of Fick's first law of diffusion and the Henry's law show the heuristic power of the concept of chemical potential. The following sections will explore a number of environmental conditions and deposit characteristics in terms of their expected effect on a substance's chemical potential.

1. Deposit Spreading. As described above, deposit spreading is a function of surface tension. A greater tissue volume underlies a given volume droplet that covers a larger area than a smaller area. The mole fraction of a substance in tissues after a given quantity of the chemical has diffused from the deposit will be lower under a large deposit area than under a small deposit area. A large deposit area should then result in greater foliar penetration by a pesticide, since the difference in chemical potential (strictly in terms of mole fraction) between the deposit and foliar tissues is greater. This relationship was found to hold by Taylor et al. (1981) and Bentson (1989), but not by Whitehouse et al. (1982) or Zabkiewicz et al. (1988). Clearly, other factors must play a role in movement of substances from deposits into foliar tissues.

A larger deposit area might be expected to result in greater volatility, depending on the chemical potential of a substance in the atmosphere versus in the deposit. No research on the relation between deposit spreading and volatility appears in the literature.

2. Concentration. Higher concentrations of a substance in deposits results in large amounts of an herbicide penetrating into tissue (Richardson and Grant 1977; Wills 1984). This is the direct result of the chemical potential being higher at greater solute concentrations in the deposit. The chemical potential of a substance in leaf tissues may rise more rapidly with a given flux of a substance into tissues, than the decline in the chemical potential in the deposit from the loss of the material, because the activities of the substance will be different in each compartment. This would explain an increase in penetration not being proportional to increases in initial concentration of substances in deposits. Some substances may have negative activity coefficients in certain solutions, which could cause less penetration of a substance into foliage at higher concentrations than at lower concentrations.

There is little information to support conjectures about the effect an increase in concentration of substances in foliar deposits would have on their volatility. From the notion of chemical potential, however, we can speculate that volatilization of a substance should increase with an increased concentration in the deposit, with the same rationale as used for penetration.

3. Formulation. The pesticide formulation will have a profound effect on a substance's penetration into foliage and volatilization. The formulation and epicuticular waxes on leaf surfaces determine the chemical potential of a substance in deposits and thus its rate of diffusion into the foliar and atmospheric compartments (Freed and Witt 1969).

McCall et al. (1986b) show that movement of atrazine depends on the phase that atrazine is in. Atrazine on leaf surfaces is in a solid phase and must change phase to penetrate into foliage. This change of phase is a discrete rate component in the models that they devised. This shows the importance in developing protocols and models of environmental fate of taking into consideration the physical properties of a substance while it is in the deposit.

Formulation components, in addition to the pesticide or substance of interest, are also penetrating into foliage and volatilizing. Formulation constituents may be involved in photolysis and other degradative pathways. The effect of dissipation of formulation components would be to change the mole fraction and activity of any other substance in the deposit and, thus, their chemical potentials. Penetration of surfactants and solvents into foliage has not received much attention. Formulation components may be important to consider in evaluating the penetration of substances into foliage, because this may alter the chemical potential of a substance in the tissues beneath the deposit.

4. Temperature. The effect of temperature has been discussed previously for both the diffusion coefficient and chemical potential. Temperatures has been somewhat neglected, both in the study of foliar penetration and in field studies of volatilization. Foliar penetration and volatilization should be studied simultaneously to accurately characterize the effects of temperature on the environmental fate of a substance initially in a deposit on foliage.

5. Humidity. Changes in humidity would change the chemical potential of a substance in the deposit if some of the deposit components are hygroscopic, e.g., humectants, surfactants, etc. Increased or decreased humidity may change the mole fractions of substances in deposits, and the physical qualities of deposits in terms of hydrophobicity. These effects would in turn change chemical potentials of substances in deposits.

Humidity may also affect the physiology of the leaf, particularly stomatal aperature. Hydration of certain cuticular components and structures may enhance penetration of some ionic and polar substances.

6. Photodegradation. Photodegradation could affect both volatilization and foliar penetration, because it would decrease the chemical potential of a substance by decreasing its mole fraction in the deposit. This effect would depend on the photodegradation rate relative to the rates of foliar penetration and volatilization and the sign of the activity coefficient. Because the chemical potential of a chemical could be changed in the deposit by photodegradation, diffusion of a substance into the leaf and air compartments would also be changed, and the steady state quantity of the substance in tissues altered. Photoproducts also diffuse into leaf tissues and presumably the atmosphere. The presence of the photoproducts in the leaf and deposit compartments could influence the chemical potential of the parent compound in those compartments.

7. Degradation in the Leaf. Degradation of a parent compound by metabolism and other processes in leaf tissues would change the activity of the parent compound in the tissues. It should be remembered that esters are a separate chemical species from acid compounds, and thus the chemical potential of the two and their mole fractions are distinct. With high rates of compound degradation in tissues, a greater quantity of the substance would be expected to penetrate into leaf tissues. The influence of other processes such as volatilization and photodegradation might result in this behavior not being observed.

8. *Process Interactions.* The balance between foliar penetration and volatilization should be considered. For instance, a substance that volatilized rapidly into the air could reduce the amount of foliar penetration, because it decreases the concentration gradient between the deposit and leaf tissues. The opposite situation of greater foliar penetration reducing the amount of a chemical that volatilized may also occur.

The chemical potential concept, means that in the ternary leaf–deposit–air system, the rate that a compound moves from the central deposit into one compartment will influence the rate the material moves into another compartment. Degradative processes will decrease a chemical's mole fraction in the deposit, which would lower its chemical potential.

C. Fate Modeling Approaches

Modeling the environmental fate of chemicals initially within pesticide deposits on foliage is a relatively recent endeavor. Models are important, however, to predict the short-term disposition of substances from pesticide deposits on foliage into the air and leaf tissues or via degradation. The two modeling approaches used are a compartmental residue transfer model and a mass balance approach. Models will need to be developed for each combination of plant species and pesticide spray mix because of the uniqueness inherent in each situation.

McCall et al. (1986a), McCall et al. (1986b); McCall (1988), and Hamburg and McCall (1988) have used a compartment model approach. The experiments are conducted in a microcosm. Different isothermal temperature regimes are used to build the data base. Quantities of the chemical are measured in air samples, foliar tissues, and the surface deposit at different times after application. From a special analytical computer package, the rates of mass transfer between compartments and metabolism are determined. The disposition of the pesticide over time is used to determine the rates of transfer at different temperatures. Outdoor tests are then conducted to determine the actual behavior of the pesticide under field conditions to verify the laboratory results. Field experiments demonstrated that the models accurately depicted field behavior.

A controlled environment chamber has been used to determine the quantities of triclopyr penetrating foliage, remaining in surface deposits, and lost from the system in ultraviolet light and the dark (Bentson 1989). Isothermal temperature regimes were used to develop data on the losses and disposition of triclopyr. Mass balance coefficients (MBCs) were calculated: $K_{1t} = n_{Lt}/(n_{Dt} + n_{Ft})$; $K_{2t} = n_{Ft}/(n_{Dt} + n_{Lt})$ where K_{1t} is the MBC for the quantity lost at time t, K_{2t} is the

MBC of the quantity that penetrates foliage, n_{Lt} is the moles that were lost, n_{Dt} is the moles remaining in the deposit, and n_{Ft} is the moles that penetrated foliage. Derivatives of linear regressions of MBCs versus time were used to determine rate of change of the MBCs at different temperatures in the light and dark. The MBCs are dimensionless and can be used for any quantity applied, so long as the chemical concentration is the same as used experimentally. Field exposures were used to validate the laboratory data. Models accurately predicted the disposition of triclopyr under outdoor conditions.

Further work is needed in modeling the fate of chemicals initially within pesticide deposits on foliage. The ternary compartment system presents a complex chemical environment for which a developed physical chemical perspective is lacking.

D. Experimental Protocols

It is evident from preceding sections that determination of the disposition of a substance from pesticide deposits on foliage must look at many simultaneous processes. Investigations of single processes will not yield data useful for predicting environmental fate under the range of field conditions deposits are exposed. Competing processes may significantly change the rate of a single process. Therefore levels of residues in different compartments must be determined over the range of conditions and times of significant change in the field.

Environmental control requires the use of microcosms or growth chambers to develop adequate data on the short-term fate of chemicals in pesticide deposits on foliage. Isothermal conditions are desirable, because the change in residue levels in each compartment are easily quantified. Data from a number of isothermal temperature regimes is more easily accommodated in models and statistical analyses. Other factor levels, e.g., humidity, light intensity, and soil moisture, can also be controlled closely near single levels in a microcosm. Times of sampling and the total duration of experimental treatments should be chosen to depict the change in residue quantities until changes become analytically insignificant. Once the disposition of a chemical from a pesticide deposit on foliage is determined at each combination of factors and times, the most important factors can be determined. The use of factorial experimental designs for this purpose has begun to increase (Bentson 1989; Willingham and Graham 1988).

Laboratory model validation is important. Field exposures are necessary to ensure that the laboratory data are adequate and that the models accurately depict field behavior of a chemical. Field exposures may show that a factor not controlled in the laboratory is actually of significance.

VI. Conclusion

The environmental fate and dynamics of substances associated with pesticide deposits on foliage have received little attention. Foliage is often the initial site of pesticide deposition. The dynamics of pesticide dissipation and degradation in association with foliar deposits is crucial in determining the ultimate fate of pesticides and other substances in the environment. Where there has been considerable development of theory and analytical methodologies for modeling the environmental fate of substances in soils, the atmosphere, and water, virtually no development has occurred for materials associated with foliar deposits. Much of the research to date on processes associated with the fate of substances in foliar deposits has been flawed in terms of lack of (1) specificity of the residue detected, (2) the source of the residues, (3) control or monitoring of meteorological and other environmental conditions, or (4) consideration of other processes besides those under investigation.

The subject of environmental fate of substances in pesticide deposits on foliage will be a fruitful area of future research. Further study should greatly increase our understanding of this aspect of the environmental fate of pesticides. Models developed from such research will be useful for evaluating foliar penetration of herbicides and other xenobiotic substances, the prediction of dislodgeable residue quantities remaining after various times under specific environmental regimes, and ultimately the development of better exposure assessments for sensitive organisms, and people.

Summary

The literature on the fate of chemicals in pesticide deposits on foliage is reviewed for foliar penetration, volatilization, and photodegradation. The literature on foliar penetration of chemicals, primarily herbicides, is well developed. The environmental fate of substances, however, is not considered in most studies of foliar penetration. Foliar penetration is often studied with herbicides in deposits that are not typical of those applied in the field. Plant material is frequently grown in a greenhouse or growth chamber. The effects of temperature and humidity are rarely studied for foliar penetration. Therefore most information that is generated from foliar penetration studies does not represent the actual behavior a substance would show in the field.

Volatilization and photodegradation of substances in pesticide deposits on foliage have not been the focus of much research. Volatilization and photodegradation can potentially alter the foliar penetration of herbicides, and significantly affect the disposition of chemicals from deposits on foliage. Integrated study of foliar penetration, volatilization, and photodegradation is necessary to accurately describe the field behavior of substances and to develop reentry guidelines.

The concept of chemical potential is a tool for generating hypotheses and in the development of experimental protocols to evaluate the fate of chemicals in pesticide deposits on foliage. Several recent protocols and modeling techniques that have been used to study the fate of substances in foliar pesticide deposits are discussed.

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