6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Pyrethrins and pyrethroids have been identified in at least 5 and 2 of the 1,636 hazardous waste sites, respectively, that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2003). However, the number of sites evaluated for pyrethrins and pyrethroids is not known. The frequency of these sites can be seen in Figure 6-1 and 6-2, respectively. All of these sites are located within the United States.

Pyrethrum is the natural extract derived from the flowers of *Chrysanthemum cinerariaefolium* and *Chrysanthemum cineum* (Metcalf 1995). Pyrethrum has long been recognized as possessing insecticidal properties, and the manufacture of flea and louse powders employing this extract began in Asia around 1800. The six active insecticidal compounds of pyrethrum are called pyrethrins. The individual pyrethrins are pyrethrin I, pyrethrin II, cinerin I, cinerin II, jasmolin I, and jasmolin II. These compounds are esters of two carboxylic acids (chrysanthemic acid and pyrethric acid) and three cyclopentenolones (pyrethrolone, cinerolone, and jasmolone). See Chapter 4 for the structures as well as the chemical and physical properties of these compounds. Synthetic pyrethroids are a diverse class of over 1,000 powerful insecticides that are structurally similar to the pyrethrins (Mueller-Beilschmidt 1990). Although they are based on the chemical structure and biological activity of the pyrethrins, the development of synthetic pyrethroids has involved extensive chemical modifications that make these compounds more toxic and less degradable in the environment. Products containing small amounts of pyrethroids for uses around the home are still classified as general use pesticides; however, emulsified or granular concentrate formulations that are applied to fields were classified as restricted use pesticides by the EPA in 1995 (EPA 2000a). The restricted use classification restricts a pesticide to be used only by a certified applicator, or under the direct supervision of a certified applicator. Although many pyrethroids have been developed, less than a dozen are used with any frequency in the United States, with permethrin being the most commonly employed pyrethroid.

Pyrethrins and pyrethroids are released to the environment primarily as a result of their use as insecticides. These compounds are very important insecticides because of their rapid paralysis of flying insects, relatively low mammalian toxicity, and rapid rate of degradation in the environment. Often,

Figure 6-1. Frequency of NPL Sites with Pyrethrins Contamination

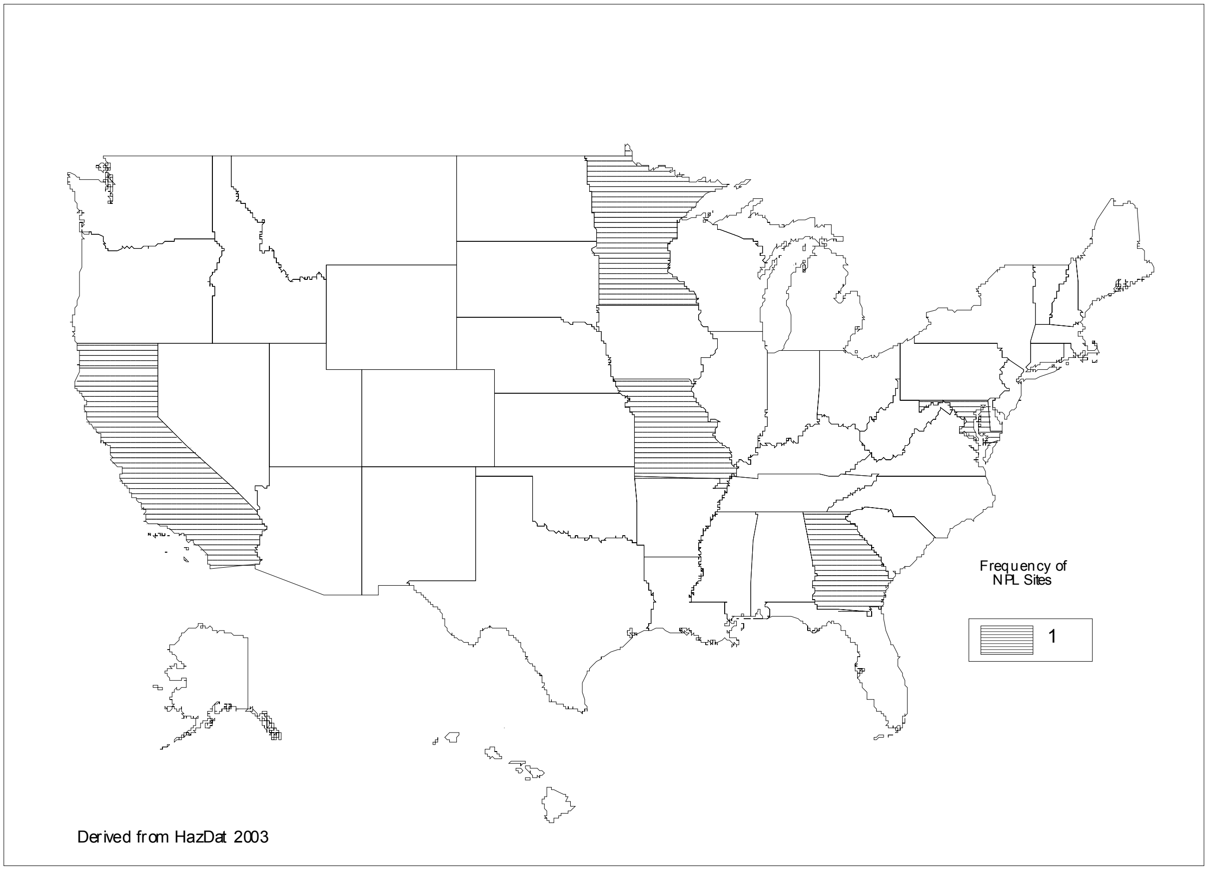
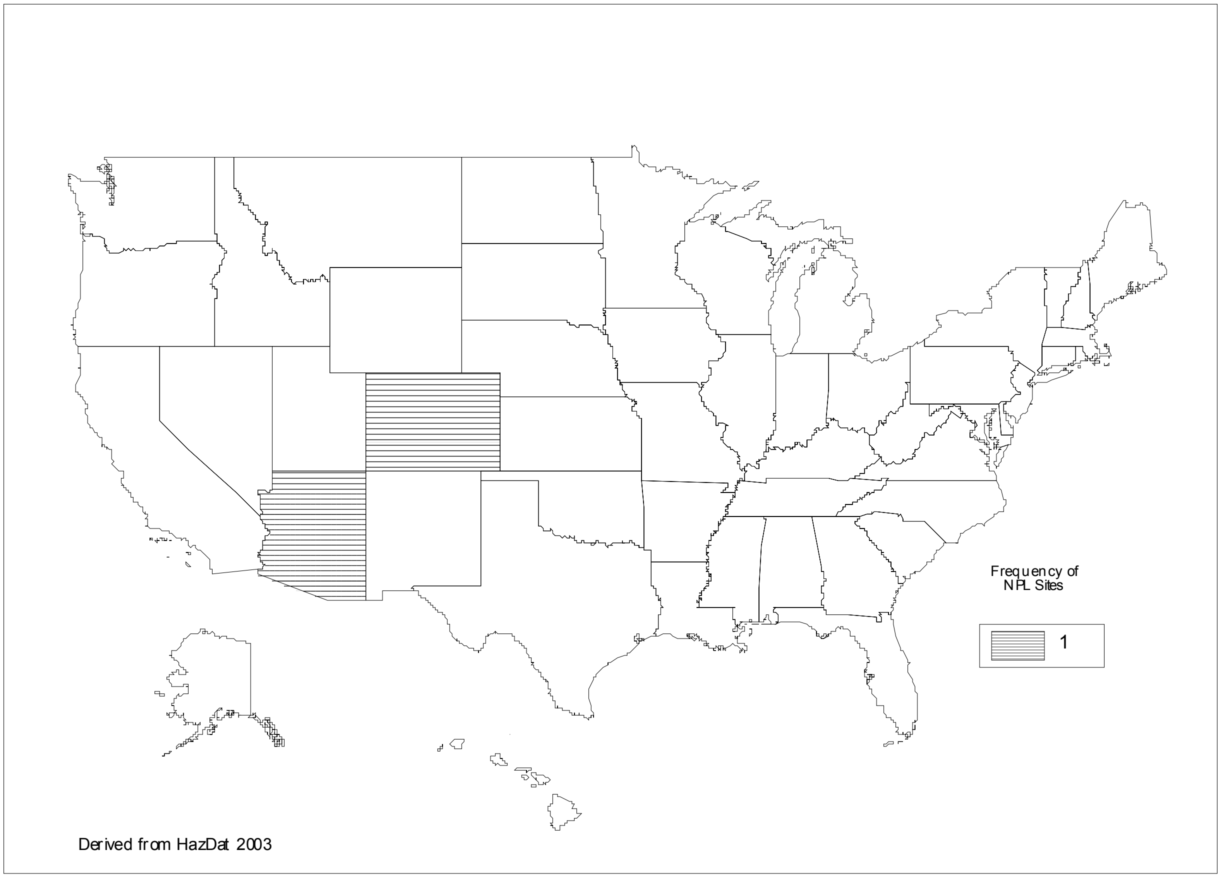


Figure 6-2. Frequency of NPL Sites with Pyrethroid Contamination



pyrethrins and pyrethroids are formulated with compounds such as piperonyl butoxide, piperonyl sulfoxide, and sesamex, which act as synergists to increase the effectiveness of the insecticide.

Pyrethrins are rapidly detoxified by enzymes of insects, and often, the paralyzed insect may survive and recover neurological function before mortality. The synergists are relatively nontoxic by themselves, but prevent the insect from detoxifying the active insecticide, thus increasing their effectiveness. At sufficient levels, the synergists may also increase the toxicity of pyrethrins and some pyrethroids in mammals. Pyrethrins are largely used indoors against flying insects in sprays, pet shampoos, and aerosol bombs, which contain about 0.04–0.25% of active ingredient and about 5–10 times this amount of piperonyl butoxide or other synergists to attenuate detoxification (Metcalf 1989). They also can be employed in multi-purpose insecticides for use on livestock, grains, fruits, and vegetables. Since the pyrethrins are not very stable when exposed to sunlight, their outdoor use on crops has diminished as relatively light-stable pyrethroids have been developed. The different pyrethroids are used in many ways to control a wide variety of insects on crops, pets, and livestock. The toxicity of the pyrethroids is influenced by the isomeric properties of the compound. For pyrethroids possessing the cyclopropane moiety, the trans isomers tend to be rapidly eliminated by mammals and possess less toxicity than the cis isomers. For example, the oral LD_{50} (rats) of 1R cis resmethrin is about 168 mg/kg, but the value for the 1R trans isomer is >8,000 mg/kg (Dorman and Beasley 1991). Pyrethroids that contain the alpha-S-cyano phenoxybenzyl alcohol moiety demonstrate considerably greater toxicity when compared to the R configuration (Dorman and Beasley 1991). The enhanced insecticidal activity of esfenvalerate over fenvalerate is one example of this (Tomlin 1997). Esfenvalerate has become the preferred compound in the United States because it requires lower application rates than fenvalerate and is thus a more powerful insecticide. Esfenvalerate contains a much higher percentage of the alpha-S-cyano phenoxybenzyl alcohol isomer than fenvalerate. For most of the pyrethroids discussed, the approximate isomeric ratios of the technical-grade products have been reported by Tomlin (1997).

Technical-grade (concentrated) pyrethrins and pyrethroids are usually formulated (mixed with carriers and solvents) for use in commercial products, and the toxicity of the formulated commercial product is not necessarily identical to the toxicity of the pure material. Inert ingredients and contaminants in pyrethroid formulations often contain suspected carcinogens or chemicals that depress the central nervous system (Mueller-Beilschmidt 1990). The EPA publishes a complete list of all inert ingredients found in pesticide products registered in the United States, and categorizes them along the following four classes: (1) inert ingredients of toxicological concern; (2) potentially toxic inert ingredients; (3) inert ingredients of unknown toxicity; and (4) inerts of minimal concern (EPA 2003). Under federal law, inert ingredients are not required to be disclosed on pesticides labels unless they contain a class one inert ingredient. Even though the EPA publishes a list of all inert ingredients used in currently registered pesticides, it does not specify the identity or quantity of inert ingredients that are used in a specific formulation.

The most important route of exposure to pyrethrins and pyrethroids for the general population is through the ingestion of foods, especially vegetables and fruits that have been sprayed with these insecticides. Farmers, pesticide applicators, and persons using these insecticides on a regular basis may also receive additional exposure through inhalation and dermal contact. Many of these compounds are employed in household products such as pet shampoos, household sprays, mosquito repellents, and lice treatments, and the general population can be exposed to these compounds through these uses.

The natural pyrethrins and many pyrethroids are rapidly degraded in the environment via photolysis, hydrolysis, and biodegradation. The environmental persistence times of many of these compounds are in the range of 1–2 days. The least persistent pyrethroids are allethrin, phenothrin, resmethrin, and tetramethrin. Structural modifications have made certain pyrethroids such as permethrin, cypermethrin, cyfluthrin, cyhalothrin, deltamethrin, fenvalerate, tefluthrin, and tralomethrin more persistent. For this reason, these compounds are utilized more often outdoors on crops than the relatively light-unstable pyrethroids and pyrethrins. Pyrethrins and pyrethroids are extremely toxic to fish and environmentally beneficial insects such as bees. In field situations, the hazard to bees is often lessened because bees are repelled by pyrethroids, which reduces their contact with plant surfaces that have recently been sprayed and decreases the chance of receiving a lethal dose. The natural pyrethrins and several pyrethroids are relatively nontoxic to mammals, but some pyrethroids such as deltamethrin, flucythrinate, cyhalothrin, permethrin, and tefluthrin have demonstrated considerable toxicity (Metcalf 1995). For example, flea applications containing a high concentration of permethrin made for use on dogs have often been associated with the accidental poisoning of cats when improperly used.

In soils, these compounds adsorb strongly and do not leach appreciably into groundwater. These compounds are not considerably taken up by the roots of vascular plants; however, they are deposited upon the leafy region of vegetation following spraying. In general, most of these compounds have relatively low vapor pressures and Henry's law constants, and as a result, volatilization from soil and water surfaces occurs slowly. Volatilization from foliage and household surfaces such as glass windows or floors occurs more rapidly since these compounds do not adhere to these surfaces as strongly in comparison to soils.

6.2 RELEASES TO THE ENVIRONMENT

Pyrethrum is found naturally in the environment as a constituent of *Chrysanthemum cinerariaefolium* and *Chrysanthemum cineum* (Metcalf 1995). However, the majority of releases of pyrethrins and pyrethroids are due to their use as insecticides. The estimated amounts of bifenthrin, cyfluthrin, cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, fenvalerate, permethrin, tefluthrin, and tralomethrin applied to crops in the United States in 1992 and 1997 are summarized in Table 6-1 (Gianessi and Silvers 2000). No data were identified for any other pyrethroid or any of the pyrethrins. Similar findings have been reported by the United States Geological Survey (USGS) 1992 Census of Agriculture (USGS 2001) (See Table 5-4).

6.2.1 Air

Releases to the air represent the most important emission pathway of pyrethrins and pyrethroids. Most applications of these insecticides involve aerial or ground spraying of crops or other vegetation, as well as the use of aerosol bombs and sprays indoors.

Manufacturing facilities may also release pyrethrins and pyrethroids during their production. A list of chemicals has been compiled for which releases are required to be reported to the EPA for the SARA Section 313 Toxics Release Inventory (TRI) (EPA 1995). The only pyrethroids that are on the list are allethrin, bifenthrin, cyfluthrin, cyhalothrin, fenpropathrin, fluvalinate, permethrin, phenothrin, resmethrin, and tetramethrin (TRI99 2001). Furthermore, data have only been reported for bifenthrin, cyfluthrin, permethrin, resmethrin, and tetramethrin. According to the TRI (Table 6-2), an estimated total of 546 pounds of bifenthrin, 16 pounds of cyfluthrin, 2,593 pounds of permethrin, 22 pounds of resmethrin, and 10,080 pounds of tetramethrin were discharged to air from manufacturing and processing facilities in the United States in 1999 (TRI99 2001). The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

Pyrethrins or pyrethroids were not detected in air at the 1,636 NPL hazardous waste sites (HazDat 2003).

Table 6-1. Trends of National Pyrethroid Use

Pyrethroid	Amounts applied (pounds) 1992	Amounts applied (pounds) 1997	Percent change
Bifenthrin	116,716	110,246	-5
Cyfluthrin	124,360	177,782	+43
lambda Cyhalothrin	205,329	321,284	+57
Cypermethrin	228,082	187,991	-18
Deltamethrin	0	27,045	
Esfenvalerate	331,522	228,885	-31
Fenpropathrin	66,368	31,839	-49
Fenvalerate	66,281	0	-100
Permethrin	1,068,598	1,066,056	-1
Tefluthrin	238,429	576,865	+142
Tralomethrin	60,105	23,767	-60

Source: Gianessi and Silvers 2000

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Pyrethroids

		Reported amounts released in pounds per year[a]						
State[b]	Number of facilities	Air[c]	Water	Underground injection	Land	Total on-site release[d]	Total off-site release[e]	Total on- and off-site release
Bifenthrin								
FL	1	36	0	No data	No data	36	No data	36
IL	1	10	No data	No data	No data	10	No data	10
MD	1	No data	No data	No data	No data	No data	No data	No data
NY	1	No data	No data	No data	No data	No data	No data	No data
TX	1	500	No data	No data	No data	500	No data	500
Total	5	546	0	0	0	546	0	546
Cyfluthrin								
MD	1	No data	No data	No data	No data	No data	No data	No data
MO	1	11	72	No data	No data	83	No data	83
NJ	1	No data	No data	No data	No data	No data	No data	No data
TX	2	5	No data	No data	No data	5	No data	5
Total	5	16	72	0	0	88	0	88
Permethrin								
AL	1	497	0	No data	No data	497	4	501
AR	2	500	No data	No data	No data	500	1,235	1,735
AZ	1	No data	No data	No data	No data	No data	No data	No data
FL	1	193	0	No data	No data	193	No data	193
GA	2	1	No data	No data	No data	1	No data	1
IL	2	10	No data	No data	No data	10	No data	10
LA	2	10	No data	No data	31,000	31,010	No data	31,010
MD	1	10	0	No data	No data	10	No data	10
MN	1	No data	No data	No data	No data	No data	No data	No data
MO	2	No data	No data	No data	No data	No data	No data	No data
NJ	1	No data	No data	No data	No data	No data	No data	No data
TN	1	751	No data	No data	No data	751	No data	751
TX	4	621	No data	No data	No data	621	No data	621
WI	1	0	No data	No data	No data	0	No data	0

Table 6-2. Releases to the Environment from Facilities that Produce, Process, or Use Pyrethroids

		Reported amounts released in pounds per year[a]						
State[b]	Number of facilities	Air[c]	Water	Underground injection	Land	Total on-site release[d]	Total off-site release[e]	Total on- and off-site release
Total	22	2,593	0	0	31,000	33,593	1,239	34,832
Resmethrin								
GA	1	No data	No data	No data	No data	No data	No data	No data
MO	1	No data	No data	No data	No data	No data	No data	No data
TX	1	22	No data	No data	No data	22	No data	22
Total	3	22	0	0	0	22	0	22
Tetramethrin								
IN	1	10,080	No data	No data	No data	10,080	No data	10,080
MN	1	No data	No data	No data	No data	No data	No data	No data
MO	1	No data	No data	No data	No data	No data	No data	No data
WI	1	0	No data	No data	No data	0	No data	0
Total	4	10,080	0	0	0	10,080	0	10,080
Grand Total	39	13,257	72	0	31,000	44,329	1,239	45,568

[a] Data in TRI are maximum amounts released by each facility.
[b] Post office state abbreviations are used.
[c] The sum of fugitive and stack releases are included in releases to air by a given facility.
[d] The sum of all releases of the chemical to air, land, water, and underground injection wells.
[e] Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

Source: TRI99 2001

6.2.2 Water

Direct releases to water are expected to be low for pyrethrins and pyrethroids because these compounds are primarily applied aerially or from ground-based sprayers directly to crops and vegetation. Spray drift following the application of these compounds, however, may contaminate nearby waters. Pyrethroids such as resmethrin, phenothrin, and permethrin, which are often used in mosquito control, are prohibited from being applied to open water or within 100 feet of lakes, rivers, and streams due to their high toxicity to fish (EPA 2000b).

Runoff water from fields or waste water from manufacturing facilities may contain pyrethrins and pyrethroids. For example, pyrethrin I and II were detected in runoff water following the application of a multi-purpose insecticide containing pyrethrins to a field in Franklin County, Kentucky (Antonious et al. 1997). Leachate collected near a pesticide manufacturing plant in Barcelona, Spain contained cypermethrin at concentrations exceeding 5–10 ppm (Rivera et al. 1985). Fenvalerate was detected in runoff water from an agricultural region in the Nicolet River Basin of Quebec, Canada at an average concentration of 0.05 μg/L in June of 1989 (Caux et al. 1996).

According to the TRI, an estimated total of 72 pounds of cyfluthrin (Table 6-2) was discharged to water from manufacturing and processing facilities in the United States in 1999 (TRI99 2001). The data listed in the TRI should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

Pyrethrins or pyrethroids were not detected in groundwater or surface water at the 1,636 NPL hazardous waste sites (HazDat 2003).

6.2.3 Soil

Releases of pyrethrins and pyrethroids to soils typically result from deposition following aerial or boom spraying of crops or vegetation. Improper disposal also may account for some sources in soil.

According to the TRI, 31,000 pounds of permethrin were discharged to land from manufacturing and processing facilities in the United States in 1999 (TRI99 2001). The data listed in the TRI should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list.

Pyrethrins were detected in soil collected at two of the NPL hazardous waste sites where it was detected in some environmental media (HazDat 2003). Pyrethroids were not detected in soil at the 1,636 NPL hazardous waste sites.

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

Spray drift following the application of any pesticide is an important source of environmental contamination and is responsible for much of the aerial transport of these compounds. Spray drift is simply the movement of the applied insecticide outside the intended target area by mass transport or diffusion. The characteristics of spray drift are influenced largely by meteorologic conditions and the method of application. Wind velocity is the dominant environmental factor that affects spray drift. Droplet size, height of flight, aircraft speed, and boom length are the dominant spraying and equipment factors that affect spray drift. Application parameters can be optimized, but they are different for different insecticides (e.g., some insecticides are more effective with large droplets and/or high spray rates and others are more effective with small droplets and/or low spray rates). In an aerial deposition study of deltamethrin involving spray application from an airplane, peak deposition to the ground was 0.5–1.2 ng/cm^2 (Johnstone et al. 1987). A site 4 km away from the spray zone received ground depositions as high as 0.2 ng/cm^2, although most areas outside the spray zone received insignificant deposition. During application of insecticides to an apple orchard in Massachusetts approximately 1 acre in size, fenvalerate was detected downwind of the spray zone (75 feet away) at a maximum concentration of 1.28 μg/m^3 (Clark et al. 1991). Within 2 hours, the level had been reduced to 0.03 μg/m^3.

Based on the vapor pressure of the pyrethrins and pyrethroids (Tables 4-4 and 4-5, respectively), these compounds are expected to exist in both vapor and particulate phases in the ambient atmosphere. Vapor phase pyrethrins and pyrethroids are rapidly degraded in the atmosphere by direct photolysis and reaction with oxidants found in air such as photochemically-produced hydroxyl radicals, ozone, and nitrate radicals. Particulate phase compounds are slower to degrade, however, and can travel long distances before being removed from the air by wet and dry deposition. The concentrations of 13 different pesticides in the atmosphere and rainfall were studied in an area of eastern France in 1992 (Millet et al. 1997). Fenpropathrin was detected in the vapor phase at concentrations ranging from 0.03 to 2.7 ng/mL and in the particulate-phase at concentrations of 0.03–4 ng/mL (Millet et al. 1997).

Pyrethrins and pyrethroids are strongly adsorbed to soil surfaces and are not considered very mobile. A wide range of K_{oc} values has been reported by different authors, but most of these values indicate a high degree of adsorption and little leaching potential. The K_{oc} values for the pyrethrins were estimated to range from 700 (cinerin II) to 27,200 (pyrethrin I) (Crosby 1995). Adsorption data are available for several pyrethroids from the U.S. Department of Agriculture Pesticide Database (USDA 2001a). The K_{oc} values for permethrin range from 10,471 to 86,000. The K_{oc} values in silt loam, sandy loam, sediment, and sand were 19,340, 20,865, 44,070, and 60,870, respectively. The K_{oc} values of cypermethrin in loamy sand (pH 5.4, 2.1% organic matter), sandy loam (pH 6.5, 3.4% organic matter), silt loam (pH 5.6, 2.0% organic matter), loamy sand (pH 4.7, 15.6% organic matter), and loam (pH 7.1, 5.2% organic matter) were 160,000; 84,000; 22,000; 34,000; and 5,800, respectively (USDA 2001a). The K_{oc} values were 3,700 to 64,125, 1,000 to 12,000, and 5,000 to 340,000 for cyfluthrin, fenvalerate, and fenpropathrin, respectively. The movement of deltamethrin, cypermethrin, permethrin, and their degradation products were studied in clay and loamy sands (Kaufman et al. 1981). Deltamethrin, permethrin (both cis and trans isomers) and cypermethrin (both cis and trans isomers), were considered immobile in all soils tested. The degradation products studied, cis, trans 3-(2,3-dichloroethenyl)-2,2-dimethylcyclopropanecarboxylate; 3-phenoxybenzyl alcohol; and 3-phenoxybenzoic acid showed some level of mobility.

Volatilization from water and soil is expected to occur slowly for many of the pyrethroids since these compounds generally have low vapor pressures and Henry's law constants (Table 4-5). When released to water, partitioning to suspended solids and sediment occurs rapidly. These compounds adsorb strongly to suspended solids and sediment in the water column, and this process significantly attenuates volatilization. Laboratory studies indicated that >95% of an initially applied amount of permethrin was adsorbed onto lake sediment and only 7–9% of the adsorbed complex could be desorbed from the sediment following four successive rinses with distilled water (Sharom and Solomon 1981). Compounds with relatively large Henry's law constants, such as deltamethrin, volatilize more readily from water surfaces than other pyrethroids. Muir et al. (1985) determined that after deltamethrin was applied to ponds, approximately 6% volatilized over the course of a 2-day incubation period. However, the major partitioning process was adsorption to suspended solids and sediment. Maguire et al. (1989) observed that deltamethrin applied to a pond in Canada was rapidly dissipated by photolysis, hydrolysis, and volatilization. Laboratory studies using sterilized pond water showed that volatilization losses increased if the deltamethrin was sprayed directly onto the surface of the water rather than injecting the solution into the subsurface water. Volatilization losses from foliage may be considerably greater than volatilization from soils because pyrethrins and pyrethroids do not adsorb as strongly to the leafy component of vegetation as to soils (Boehncke et al. 1990). Laboratory and field tests were conducted to evaluate volatilization losses of deltamethrin sprayed on plant and soil surfaces (Boehncke et al. 1990). Under the summer time conditions of the field tests, mean evaporative losses from lettuce, kohlrabi, green beans, and summer wheat ranged from 12 to 71% over a 24-hour period, while evaporative losses from soil were approximately 24% in 24 hours. Since pyrethrin I, cinerin I, and jasmolin I have larger Henry's law constants than the corresponding esters (pyrethrin II, cinerin II, and jasmolin II), they are expected to volatilize from moist soils and water more rapidly. The estimated volatilization half-lives of pyrethrin I, cinerin I, and jasmolin I from soil range from 1.8 to 2.7 days, while the half-life values for pyrethrin II, cinerin II, and jasmolin II range from 36.8 to 97 days (Crosby 1995). Pyrethrins and pyrethroids are often used indoors in sprays or aerosol bombs, and the volatilization rates from glass or floor surfaces may be significantly faster than from soils since these compounds are not likely to adsorb as strongly to these surfaces.

Pyrethrins and pyrethroids can bioconcentrate in aquatic organisms and are extremely toxic to fish. The bioconcentration factor (BCF) of permethrin, fenvalerate, deltamethrin, and cypermethrin in rainbow trout (*Oncorhynchus mykiss*) and sheepshead minnow (*Cyprinodon variegatus*) were approximately 450–600, 180–600, 100–1,200 and 120–400, respectively (Haitzer et al. 1998). The BCF values varied considerably as the amount of dissolved organic matter in the water column was changed (Haitzer et al. 1998). The steady-state BCF values of fenvalerate and permethrin in eastern oysters (*Crassostrea virginica)* were measured as 4,700 and 1,900, respectively, over a 28-day incubation period (Schimmel et al. 1983). In pesticide-free water, the contaminated oysters depurated permethrin and fenvalerate to nondetectable levels in 1 week. Insect BCF values after 6 hours of exposure to sublethal permethrin concentrations were 18, 30, 7, 4, and 24 for black fly, caddisfly, damsefly, water scavenger, and mayfly, respectively (Tang and Siegfried 1996). Using a static test system and a 3-day incubation period, the BCF value for cypermethrin in golden ide fish (*Leuciscus idus melanotus*) was measured as 420 (Freitag et al. 1985). In a series of field tests designed to simulate the environmental fate of tralomethrin and deltamethrin due to spray drift and field runoff, fathead minnows were exposed to different levels of these pyrethroids (Erstfeld 1999). Over the course of a 7-day incubation period, the minnows were analyzed and BCF values of 219 and 315 were calculated for days 4 and 7, respectively, for the tralomethrin spray drift pond microcosms. The BCF values were 185 and 143 for days 4 and 7, respectively, for the tralomethrin runoff water microcosms. The BCF values were 260 and 185 for days 4 and 7, respectively, for the deltamethrin spray drift pond microcosms and the BCF values were 169 and 166 for days 4 and 7, respectively, for the deltamethrin runoff water microcosms.

Little data exist regarding the uptake and transport of pyrethrins and pyrethroids by plant material. Since many of these compounds are rapidly degraded in the environment, this transport mechanism may not be an important environmental fate process other than the initial settling of these compounds on the canopy following deposition. The aerial surface of a plant, including foliage, is covered by a cuticle, which serves as a barrier to water loss and to prevent penetration of applied chemicals or environmental pollutants (Paterson et al. 1990). Once deposited on the surface, a chemical may be degraded, bind to the cuticle, or diffuse into the plant through the stomata. Parihar and Gupta (1998) demonstrated that fenvalerate applied to the surface of pigeon pea (*Cajanus cajan*) in India under field conditions was rapidly degraded and did not accumulate significantly in the plants. The fenvalerate residues were below detection limits at 15 and 20 days postapplication for two different application rates. These compounds can also be taken up from the soil by the roots of the plant. Since pyrethrins and pyrethroids adsorb strongly to soils, their uptake from roots and transport within plants is expected to be limited. Lettuce, beets, and wheat planted in soil 30, 120, and 365 days after treatment of [^{14}C]-fenvalerate were shown to accumulate very little ^{14}C when harvested at maturity (Lee 1985). Furthermore, it was demonstrated that very little downward movement of the radiolabeled fenvalerate occurred in the soils and that little, if any, fenvalerate or its degradation products are taken up by the roots of these plants. Chemicals may enter aquatic plants in solution directly from the water. Erstfeld (1999) demonstrated that aquatic plants accumulate deltamethrin and tralomethrin from the water column, in a series of pond and runoff water microcosms. Following application of tralomethrin, the BCF values in macrophytes were 18,200 and 8,290 in pond and water runoff microcosms, respectively, at 7 days postapplication (Erstfeld 1999). This observation is consistent with the data of Muir et al. (1985) that observed deltamethrin residues in aquatic plants at concentrations ranging from 253 to 1,021 ng/g 24 hours after application of 1.8–2.5 μg/L deltamethrin solution to a pond. Similarly, permethrin applied to the surface of a fast-flowing stream was taken up by aquatic plants (Sundaram 1991). Following application of 1.658 g of permethrin to the stream surface, permethrin concentrations in aquatic plants located 280 m from the application site ranged from 6.78 ng/g (420 minutes postapplication) to 17.6 ng/g (60 minutes postapplication). It was concluded that the permethrin was largely absorbed in foliar waxes in the water arum and was slowly desorbed and lost by hydrolytic or microbial degradation.

6.3.2 Transformation and Degradation

Many studies use first-order kinetics to model the dissipation of pesticides in the environment because a half-life for the chemical can be defined. The half-life represents the calculated time for loss of the first 50% of the substance. However, in many cases, the time required for the loss of the remaining substance may be substantially longer, and the rate of disappearance may decline further as time progresses. This is often the case for the disappearance of pesticides in soils. For simplicity, the term half-life in this document is used to indicate the estimated time for the initial disappearance of 50% of the compound and does not necessarily imply that first-order kinetics were observed throughout the experiment unless otherwise noted.

6.3.2.1 Air

Pyrethrins and pyrethroids in the ambient atmosphere are degraded rapidly through reaction with atmospheric oxidants or by direct photolysis. Based upon rate constants for the reaction with hydroxyl radicals and ozone molecules derived from a structure estimation method (Meylan and Howard 1993), the atmospheric half-lives of the pyrethrins are on the order of several minutes to a few hours (HSDB 2001). These compounds are also rapidly degraded by direct photolysis. Chen and Casida (1969) observed that thin films of pyrethrin I applied to glass plates underwent 90% photodecomposition within 0.2 hours, while a dark control underwent very little loss.

Pyrethroids where the isobutenyl group attached to the cyclopropane moiety has been altered are more stable to sunlight than the early pyrethroids like allethrin or resmethrin. For this reason, pyrethroids such as permethrin, deltamethrin, cyhalothrin, cyfluthrin, and cypermethrin are more frequently applied outdoors to crops in comparison to the rapidly degraded pyrethroids like resmethrin and allethrin. When exposed to daylight as a thin film indoors near a window, phenothrin decomposed with a half-life of about 6 days, whereas about 60% of applied permethrin remained undecomposed after 20 days (WHO 1990c). Thus, the replacement of the isobutenyl group with the dichlorovinyl substituent significantly enhanced the photostability of permethrin in comparison to phenothrin (WHO 1990c). The photodegradation half-life of permethrin on thin films exposed to light at 295–305 nm was in the range of 5–7 days, while the half-lives for deltamethrin and cis cypermethrin were 6 and 7.5 days, respectively (Chen et al. 1984). Cypermethrin exposed to ultraviolet (UV) light >290 nm, underwent 30.2% photomineralization over a

17-hour irradiation period (Freitag et al. 1985). The photodegradation half-life of tetramethrin on glass films exposed to a sunlamp was approximately 1 hour, with nearly 100% photodecomposition observed after 15 hours of illumination (Chen and Casida 1969). Allethrin applied to glass films was degraded approximately 90% in 8 hours when irradiated with UV light, but some of the loss was attributed to volatilization (Chen and Casida 1969). Aqueous suspensions of allethrin underwent approximately 11.1% photodecomposition after only 15 minutes of exposure to sunlight (Ivie and Casida 1971b). It was also observed that the addition of chloroplasts to the suspensions photosensitized the photolysis and increased degradation rates in sunlight, suggesting that photodegradation on crops is a very rapid process. The photolysis half-life of resmethrin films on glass plates ranged from about 20 to 90 minutes when exposed to forenoon and midday sunlight conditions (Samsonov and Makarov 1996). The fastest rates were observed during midday sunlight and in the presence of the sensitizer methylene blue. Resmethrin also underwent direct photolysis when aerosols were irradiated with sunlight. Photodecomposition products of resmethrin included chrysanthemic acid, phenylacetic acid, benzyl alcohol, benzaldehyde, benzoic acid, and various chrysanthemates (Ueda et al. 1974). Cyhalothrin was reported as being stable to light, with <10% photodecomposition after 20 months while stored under sunlight conditions (Tomlin 1997). However, on soil surfaces and in aqueous solutions at pH 5, cyhalothrin was degraded upon exposure to sunlight with a reported half-life of about 30 days (WHO 1990a).

Compounds, such as nitroanilines, that absorb light in the environmental UV spectrum have been shown to photostabilize pyrethrins and pyrethroids (Dureja et al. 1984). Following irradiation at 360 nm for 18 hours, the percent recoveries of pyrethrins, allethrin, kadethrin, resmethrin, tetramethrin, phenothrin, and fenpropathrin on silica gel plates were 1, 2, 0, 7, 2, 29, and 28%, respectively (Dureja et al. 1984). Following the addition of the herbicide trifluralin, the amounts recovered after irradiation were: pyrethrins, 54%; allethrin, 78%; kadethrin, 47%; resmethrin, 85%; tetramethrin, 77%; phenothrin, 66%; and fenpropathrin, 83% (Dureja et al. 1984). Pyrethroids with halogenated acid moieties were also protected from photodecomposition due to the addition of trifluralin. Following irradiation at 360 nm for 32 hours on silica gel plates, the percent recoveries of permethrin, cypermethrin, deltamethrin, and fenvalerate were 32, 19, 25, and 23%, respectively. With the addition of trifluralin, the percent recoveries increased to 65% for permethrin, 83% for cypermethrin, 57% for deltamethrin, and 90% for fenvalerate (Dureja et al. 1984). Deltamethrin-impregnated cotton strips were degraded upon irradiation with UV light at differing rates, depending upon the color of the fabric and whether or not a UV absorber was added to the impregnating solution (Hussain and Perschke 1991). When white cotton fabric treated with deltamethrin alone was irradiated for 24 hours, nearly 100% photodegradation was observed. However, deltamethrin applied to blue and black fabric was degraded approximately 44.9 and 37.5%, respectively, over a 24-hour irradiation period (Hussain and Perschke 1991). Addition of the UV absorber 2,4-dihydroxybenzophenone also decreased the amount of degradation following exposure to UV light.

6.3.2.2 Water

Since pyrethrins and pyrethroids undergo photolysis in the atmosphere, they are also degraded by this mechanism in sunlit surface waters. Photosensitizing agents found in natural waters such as fulvic and humic acids increase the rate of photolysis. The photolysis half-life of permethrin in seawater exposed to outdoor light was determined to be 14 days and the half-life of fenvalerate was measured as 8 days (Schimmel et al. 1983). Little change in concentration was observed when each pyrethroid was incubated in dark constant temperature controls. Photolysis half-lives of 27.1 and 19.6 hours were determined for respective cis and trans isomers of permethrin, respectively, in 800 mL of pond water exposed to sunlight (Rawn et al. 1982). The photodegradation half-life of cypermethrin in a distilled water solution ranged from 2.6 to 3.6 days and the half-lives in river and seawater were in the range of 0.6–1.0 days when exposed to sunlight (Takahashi et al. 1985a). The cis isomers underwent photodegradation at greater rates than the trans isomers. The photodegradation half-life of deltamethrin in distilled water was 1–2 days, while the half-life in river water was longer, yet still <5 days when solutions were exposed to sunlight (Maguire 1990). The photolysis half-lives of fenpropathrin in distilled water, distilled water with humic acid, river water, and seawater were 13.5, 6, 2.7, and 1.6 weeks, respectively, when exposed to sunlight (Takahashi et al. 1985c).

These compounds also undergo hydrolysis in the environment at varying rates depending upon pH and temperature. Generally, hydrolysis is only an important environmental fate process under alkaline conditions and at temperatures of 20 °C or greater. The hydrolysis half-life of cyfluthrin is about 231 days at pH 7, but about 2 days at pH 8 (USDA 2001a). At pH 5 and pH 7, permethrin is stable towards abiotic hydrolysis, but at pH 9, the abiotic hydrolysis half-life is about 50 days (USDA 2001a). The aqueous hydrolysis half-lives of cypermethrin in sterile water-ethanol (99:1) phosphate buffers at 25 °C were determined to be 99, 69, 63, and 50 weeks at pH values of 4.5, 6, 7, and 8, respectively (Chapman and Cole 1982). The half-lives of an 8 ppb solution of fluvalinate at 25 °C were 48, 22.5, and 1.13 days at pH 5, 7, and 9, respectively (Tomlin 1997). The hydrolysis of fenpropathrin in buffer solution was studied under various pH and temperature conditions (Takahashi et al. 1985b). At 25 °C, the hydrolysis half-lives of fenpropathrin were approximately 2.2 years and 8 days at pH 7 and 9, respectively (Takahashi et al. 1985b). At 40 °C, the half-lives were about 80 days and 19 hours at pH 7 and 9, respectively (Takahashi et al. 1985b).

Pyrethroids are readily degraded by environmental microorganisms. The half-life of permethrin in a sediment/seawater solution was <2.5 days, but under sterile conditions, there was no significant change in the permethrin concentration over a 4-week incubation period, suggesting that biodegradation was responsible for the loss under nonsterile conditions (Schimmel et al. 1983). The half-life of fenvalerate in the sediment/seawater solution was 27–42 days under nonsterile conditions and little loss was noted under sterilized conditions (Schimmel et al. 1983). Pond and runoff water microcosms were constructed to simulate the fate and persistence of tralomethrin and deltamethrin under field conditions following spray drift over a 7-day study period (Erstfeld 1999). The degradation profiles of tralomethrin in water showed rapid conversion to deltamethrin with a calculated half-life of about 6.8 hours. The resulting deltamethrin was further degraded to decamethrinic acid with a half-life of about 81 hours. In sediment, tralomethrin was rapidly converted to deltamethrin. Two experiments were conducted to evaluate the persistence of fenvalerate in seawater and seawater/sediment microcosms under different conditions (Cotham and Bidleman 1989). The half-lives of fenvalerate in unsterilized seawater at pH 8 and 8.05 were 17 and 14 days, respectively. The half-lives of fenvalerate in heat sterilized seawater at pH 8 and 8.05 were 41 and 33 days, respectively (Cotham and Bidleman 1989). Bioresmethrin, cypermethrin, deltamethrin, permethrin, fenvalerate, and Nuerelle DX 50 (50 grams cypermethrin and 500 grams chlorpyriphos mixture) were degraded at different rates in a model ecosystem consisting of polluted river water and sediment under aerobic conditions (Lutnicka et al. 1999). The temperature of the ecosystem was 15–19 °C and the pH was 7.7. The ranges of half-lives in the model ecosystem were: bioresmethrin, 1.2–4.6 days; cypermethrin, 4.7–30.8 days; deltamethrin, 0.5–0.8 days; permethrin, 1.1–3.6 days; fenvalerate, 3.5–4.4 days; and cypermethrin in the Nuerelle DX 50 mixture, 11.6–30.4 days (Lutnicka et al. 1999). It was also noted that the degradation rates of the pyrethroids followed first-order kinetics, and that only fenvalerate and cypermethrin residues remained at detectable levels 56 days postapplication.

No data exist regarding the degradation of pyrethrins in water. Based upon degradation studies of structurally similar esters and the degradation rates of the pyrethroids, it has been concluded that pyrethrins should degrade rapidly in water (Crosby 1995).

6.3.2.3 Sediment and Soil

Laboratory and field studies suggest that pyrethroids are degraded faster in soils than many of the long-lasting organochlorine, organophosphorus, and carbamate pesticides. Fenvalerate and deltamethrin appear to be the most persistent compounds in commercial use, especially in soils containing a high clay content or a large percentage of organic matter.

Chapman et al. (1981) studied the persistence of permethrin, cypermethrin, deltamethrin, fenpropathrin, and fenvalerate in sterile and nonsterile soils in order to assess the importance of biodegradation versus abiotic transformation mechanisms. After initial application of 1 ppm of each pyrethroid in a mineral soil, the percentages of pesticide recovered after an 8-week incubation period were: fenpropathrin, 2%; permethrin, 6%; cypermethrin, 4%; fenvalerate, 12%; and deltamethrin, 52%. Over 90% of each pyrethroid was recovered from heat sterilized soils, suggesting that biodegradation plays a crucial role in the disappearance of these compounds. Similar results were obtained in a richly organic soil, although the amounts degraded were lower over the 8-week incubation period. In the organic soil, the percent recoveries after 8 weeks were as follows: fenpropathrin, 8%; permethrin, 16%; cypermethrin, 16%; fenvalerate, 58%; and deltamethrin, 74%. The USDA Pesticide Database lists half-lives in the range of 88–287 days for fenvalerate, 56–63 days for cyfluthrin, 4–40 days for permethrin, and 6–60 days for cypermethrin in aerobic soils (USDA 2001a). In a biodegradation study using deltamethrin as the sole carbon source and pure bacterial isolates from soil as inoculum, 35.7–44.4% of the initially applied deltamethrin metabolized in 1 week and 59.7–72.5% was degraded in 2 weeks (Khan et al. 1988). In the absence of bacterial isolates, only 3–10% of the deltamethrin was degraded. Deltamethrin was applied to a sandy loam from Alberta, Canada at an initial fortification level of 17.5 g/ha (42.5 ppb) and studied under indoor laboratory conditions and field conditions over a 52-week incubation period (Hill 1983). The half-life of deltamethrin under the field conditions was 6.8 weeks, and approximately 5–7% of the applied deltamethrin remained after 52 weeks. The half-life of the deltamethrin in the indoor experiments was 4.8 weeks and the differences in persistence between the field and laboratory experiments were attributed to climate effects. In both cases, the degradation was exponential and the decay could be reasonably fit to first-order kinetic equations (Hill 1983). It was noted that in the field experiments, the rate of degradation was slowed during the winter months. The anaerobic degradation of cyfluthrin in heavy clay soils was studied under laboratory conditions for a period of 140 days at different moisture levels and organic matter content (Smith et al. 1995). The percentages of cyfluthrin recovered in an unamended soil after 31, 73, 115, and 140 days were 50.8, 27.9, 14.8, and 15%, respectively. The percentages of cyfluthrin recovered in a soil amended with organic matter from cotton plant residue were

35.2, 20.9, 14.4, and 9.4%, respectively, over the same incubation periods. The disappearance of cyfluthrin was not significantly affected by the moisture content of the soils (Smith et al. 1995). The half-lives of fluvalinate and flucythrinate in agricultural soil were 6.8–8.0 days and 9.4–11.9 days, respectively, depending upon the application rate (Agnihotri and Jain 1987). It was observed that the rate of disappearance followed first-order kinetics, and that after 40 days, neither insecticide remained at detectable levels in the soil (Agnihotri and Jain 1987). The half-lives of fenvalerate in a tidal marsh sediment ecosystem, with sediment obtained from the Chesapeake Bay, were calculated as 6.3 days (0.2 ppm initial concentration) and 8.8 days (1 ppm initial concentration) (Caplan et al. 1984). It was not possible to determine the exact mechanism of degradation (hydrolysis, biodegradation, or photolysis) since no dark or sterile controls were run; however, biodegradation and hydrolysis were the most likely routes since the fenvalerate was initially incorporated into the sediment, shielding it from substantial sunlight. The half-life of fenvalerate in a sediment/seawater (obtained from Charleston, South Carolina) system at pH 7.3–7.7 was 12 days (Cotham and Bidleman 1989). The half-life of fenvalerate applied to sandy loam and silty clay loam soils at an initial concentration of 5 ppm was approximately 75–80 days under indoor laboratory conditions (Lee 1985). The half-life under outdoor conditions was approximately 60 days (Lee 1985).

Since light is attenuated as a function of depth from the soil surface, photolysis of pyrethrins and pyrethroids is only an important environmental fate process at the surface of the soil. The photodegradation of cypermethrin was studied by exposing various soil surface applications to sunlight for 7–10 days (Takahashi et al. 1985a). The half-lives on soil surfaces exposed to sunlight ranged from 0.6 to 1.9 days, while half-lives on non-illuminated soils were >7 days. The photodegradation products resulting from exposure of cypermethrin to sunlight included various carbanoyl and hydroxy derivatives, a variety of benzoic acid derivatives, several lactone derivatives, and several aliphatic carboxylic acid derivatives (Takahashi et al. 1985a). The photodegradation of esfenvalerate on thin films of soil, clay, and humic material was studied (Katagi 1991). Half-lives ranged from about 8 to 100 days with reaction at the cyano group and ether cleavage in the alcohol moiety responsible for the photodegradation on the surfaces tested. The shortest photolysis half-lives were observed when esfenvalerate was incorporated into the clay thin films. The half-life of fenpropathrin on the surface of a sterilized sandy loam was 3–4 days following irradiation with natural sunlight (Dureja 1990). After 15 days, it was observed that only about 12% of the original amount remained (Dureja 1990).

A mid-summer field study in Alberta, Canada was performed to determine the persistence of deltamethrin on crops and litter in order to establish a minimum time interval between treatment of pastures and grazing by cattle (Hill and Johnson 1987). The average half-life of deltamethrin applied to two pastures to control grasshoppers was 5.8 days on the forage and 17 days on the litter (Hill and Johnson 1987). The authors attributed the rapid initial loss of deltamethrin to surface processes including volatilization and photolysis, but the remainder of the loss occurred by degradation through metabolic and chemical processes. The longer half-life of deltamethrin on the litter reflects a lower initial loss of the chemical through surface processes (volatilization and photolysis) due to the litter being more sheltered.

No data exist regarding the degradation rates of pyrethrins in soil. Based upon hydrolysis and biodegradation studies of structurally similar esters and the relatively rapid degradation rates of the pyrethroids, it has been concluded that pyrethrins should degrade rapidly in soil (Crosby 1995).

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Pyrethrins and pyrethroids have been detected at low levels in ambient air, indoor air samples, surface water, groundwater, and drinking water. These compounds have also been detected in soils, sediment, various foods, and animals. Quantitative concentration information is presented in the following sections.

6.4.1 Air

Pyrethrins and pyrethroids are used in both indoor and outdoor settings to control insects; therefore, these compounds are frequently detected in the air of homes and buildings after their use. During a study of pesticide use in Florida, permethrin was qualitatively identified in the porch or patio of two out of eight homes in Jacksonville, during August of 1985 (Lewis et al. 1988). During a study of pesticide occurrence in indoor air of New Jersey households, permethrin was detected at concentrations of 2,550 ng/g (cis) and 3,850 ng/g (trans) in household dust immediately following its application as an aerosol flea treatment (Roinestad et al. 1993). The concentrations decreased to 550 ng/g (cis) and 675 ng/g (trans) 8 weeks postapplication. Permethrin, resmethrin, and cypermethrin were detected in the ambient air of commercial pest control buildings in North Carolina at concentration ranges of 0.03–2.34, 0.31–14.10, and 0.02–11.66 $\mu g/m^3$, respectively (Wright et al. 1996). The concentrations of cypermethrin detected in the air of vacant dormitory rooms following its application for cockroach control were 18.2, 8.5, 3.0, 7.1, 4.4, 0.6, and 0.3 $\mu g/m^3$ at 0, 7, 28, 42, 56, 70, and 84 days postapplication, respectively (Wright et al. 1993). The concentration in untreated rooms adjacent to the sprayed rooms ranged from 0.1 $\mu g/m^3$ (84 days postapplication) to 6.4 $\mu g/m^3$ (immediately following application). The indoor air concentration of allethrin in a public community college cafeteria after bi-monthly applications ranged from 0.2 ng/m^3 (13 days after application) to 48 ng/m^3 (0.1 days after application) (Eitzer 1991). The maximum airborne residue of fenpropathrin in greenhouse air after application was 0.28 μg/m^3 (Siebers and Mattusch 1996).

The mean and maximum concentrations of vapor-phase fenpropathrin in air collected at Colmar, France between 1991 and 1993 were 0.5 and 2.7 ng/mL, respectively (Millet et al. 1997), while the mean and maximum concentrations of particulate-phase fenpropathrin in air were 0.6 and 4 ng/mL, respectively (Millet et al. 1997). The concentrations of permethrin and cypermethrin in airborne particulate matter in areas of Saudi Arabia with heavy insecticide use were 1.84–30.70 and 0.28–3.61 μg/m^3, respectively (Badawy 1998).

6.4.2 Water

Permethrin was detected in 24 of 12,253 ambient surface water samples in the United States at an average concentration of 0.0137 μg/L (EPA 2000c). Permethrin was detected 6 hours postapplication at concentrations of 0.017 and 0.018 μg/L in 2 of 6 samples from a slow-moving creek approximately 60 meters from a potato field where permethrin was applied via aerial spraying (Frank et al. 1991). Concentrations as high as 0.28 μg/L were observed 10 minutes postapplication, but decreased rapidly. In 1996, the average permethrin concentration in surface waters from agricultural areas in Thailand was 2.81 μg/L (Thapinta and Hudak 2000). The deposition of cypermethrin on the surface of three streams adjacent to vineyards in France that were sprayed (via mistblowers) with cypermethrin were in the range of 0.04–0.45 mg/m^2 and cypermethrin concentrations in subsurface water of the streams were in the range of 0.4–1.7 μg/L soon after spraying, but decreased to <0.1 μg/L within a period of about 5 hours (Crossland et al. 1982).

Since pyrethrins and pyrethroids adsorb strongly to soils, they are not often detected at elevated concentrations in groundwater and drinking water. In an EPA compilation of monitoring studies of pesticides in groundwater from 1971 to 1991, fenvalerate was detected in 5 out of 345 wells at concentrations of 0.01–0.28 μg/L and permethrin was detected in 4 out of 1,097 wells at concentrations of 0.01–1.25 μg/L (EPA 1992). Cypermethrin was not detected in 311 wells sampled, tralomethrin was not detected in 188 wells sampled, and pyrethrins were not detected in 144 wells sampled (EPA 1992). As part of the National Drinking Water Contaminant Occurrence Database, permethrin was detected in 3 of 73 ambient spring water samples at an average concentration of 0.0133 μg/L and in 3 of 5,728 ambient groundwater samples at an average concentration of 0.011 μg/L (EPA 2000c). Permethrin was not detected in 94 wells analyzed in a 1992 USGS study of pesticides in near-surface aquifers in the Midwest (Kolpin et al. 1995). In the 1993–1995 USGS survey of pesticides in shallow groundwater throughout the United States, permethrin was detected in 2 out of 1,034 sites at a maximum concentration of 0.007 μg/L (Kolpin et al. 1998).

6.4.3 Sediment and Soil

Pyrethrins and pyrethroids are detected in agricultural soils or sediment from lakes, rivers, and streams that may have been contaminated from spray drift or runoff water. Following the application of a multipurpose insecticide containing pyrethrins on a field in Franklin County Kentucky, the concentrations of pyrethrin I and II decreased in the soil as a function of time. After 1 hour, 1, 4, 8, 12, 18, 24, and 30 days, the concentrations of pyrethrin I were 9, 5.1, 3.9, 2.1, 0.9, 1.3, 0.3, and 0.8 μg/kg, respectively (Antonious et al. 1997). The concentrations of pyrethrin II over the same time frame were 900, 140, 103, 23, 1, 1, 1, and 1 μg/kg. The average concentration of permethrin in soils collected from 48 agrochemical facilities located throughout the state of Illinois was 190 μg/kg, with a range of concentrations from 11 to 4.22×10^5 μg/kg (Krapac et al. 1995). During 1996–1997, concentrations of permethrin in soil samples from cultivated areas in Thailand ranged from 62.41 to 1,178.40 μg/kg (Thapinta and Hudak 2000). Fenvalerate was detected in soil samples of two fields near the Nicolet River Basin in Quebec, Canada at concentrations of 20 and 8 μg/kg (0–5 cm depth) and 2 and 5 μg/kg (25–30 cm depth) (Caux et al. 1996). Permethrin was detected in the soil of two potato farms in Canada at concentrations ranging from 110 to 380 μg/kg at 6 hours after application via aerial spraying (Frank et al. 1991). The concentrations decreased to 6–220 μg/kg at 6 days postapplication and 8–15 μg/kg at 30 days postapplication (Frank et al. 1991).

Permethrin was detected in three of six sediment samples at concentrations of 18.1–21.1 μg/kg from a creek approximately 60 meters from a potato field where permethrin was applied via aerial spraying (Frank et al. 1991). At 30 days postapplication, permethrin was detected in only one of six samples at a concentration of 10 μg/kg (Frank et al. 1991). Sediment samples from an industrialized area of the Meltham Catchment in England contained permethrin at concentrations of 0.26–309.5 μg/kg and cyfluthrin at concentrations of 0.086–5.8 μg/kg (Yasin et al. 1996). Deltamethrin was detected in sediment samples of the Vemmenhog Catchment in Sweden at an average concentration of 20 μg/kg (Kreuger et al. 1999).

6.4.4 Other Environmental Media

According to the 1999 Food and Drug Administration (FDA) Pesticide Monitoring Program, permethrin was identified in 54 out of 1,040 food composites analyzed (FDA 2001). No range of levels was reported. Fenvalerate and fluvalinate were also qualitatively identified in food products, but no percentage of occurrence or concentrations were listed. Permethrin was also identified in 10 out of 78 baby foods at concentrations of 0.6–60 μg/kg and fenvalerate was identified in 1 out of 78 baby foods at a concentration of 5 μg/kg (FDA 2001). Resmethrin has been identified, but not quantified, in corn, cornmeal, flour, and wheat (Simonaitis and Cail 1975). An FDA analysis of 320 food groups conducted from 1991 to 1999 determined that pyrethroids were present at varying levels in several foods. The results of this study pertaining to pyrethroids are summarized in Table 6-3 (FDA 2000c).

Cypermethrin was detected in the milk from cows wearing ear tags impregnated with cypermethrin to control horn flies and other insects (Braun et al. 1985). Over a 21-day period, 60 milk samples were obtained from 10 cows. Only 11 out of 60 butterfat samples contained cypermethrin above the detection limit of 4 μg/kg. The range of concentrations in the butterfat of these 11 samples was 4.0–9.6 μg/kg (Braun et al. 1985). Flumethrin, deltamethrin, cypermethrin, and cyhalothrin were detected in the milk of 10 dairy cows after single dermal applications at recommended doses (Bissacot and Vassilieff 1997a). The highest mean concentration for flumethrin was observed 28 days postapplication, while the highest mean concentrations for cypermethrin and cyhalothrin were observed 1 day postapplication. The highest mean concentration of deltamethrin in the milk was observed 7 days postapplication.

Fenvalerate residues were detected in a variety of nontarget vertebrate and invertebrate species after application onto a cotton field to control bollworm and tobacco budworm (Bennet et al. 1983). Terrestrial invertebrates contained the lowest levels, while the highest residue concentrations were found in fish and insects. Fenvalerate levels in ppm were as follows: house mouse, 0.01; dickcissel, 0.02; ribbon snake, 0.12; toad, 0.02; golden shiner, 0.47; mosquitofish, 0.32; snail, 0.53; and ground beetle, 0.55 (Bennett et al. 1983).

Table 6-3. Levels of Pyrethroids Detected in Foods

Pyrethroid	Food item	n	Mean (ppm)	Minimum (ppm)	Maximum (ppm)
Bifenthrin	Raw strawberries	3	0.0487	0.0040	0.084
Cyfluthrin	Green peppers	1	0.002	0.002	0.002
Cyfluthrin	Raw raddish	1	0.013	0.013	0.013
Cyfluthrin	Beef chow mein	1	0.004	0.004	0.004
lambda cyhalothrin	Tomato sauce	1	0.003	0.003	0.003
lambda cyhalothrin	Green peppers	1	0.01	0.01	0.01
lambda cyhalothrin	Stuffed peppers	1	0.002	0.002	0.002
Cypermethrin	Broccoli	1	0.0013	0.0013	0.0013
Cypermethrin	Collards	7	0.442	0.052	1.247
Cypermethrin	Iceberg lettuce	2	0.0185	0.013	0.024
Esfenvalerate	Collards	4	0.0535	0.021	0.099
Esfenvalerate	Raw tomatoes	5	0.0146	0.005	0.02
Esfenvalerate	Green peppers	4	0.015	0.009	0.024
Esfenvalerate	Catsup	1	0.002	0.002	0.002
Esfenvalerate	Strained peaches/junior	2	0.0065	0.005	0.008
Esfenvalerate	Fruit dessert/junior	2	0.0025	0.002	0.003
Esfenvalerate	Raw apricot	1	0.06	0.06	0.06
Esfenvalerate	Mushrooms	1	0.019	0.019	0.019
Esfenvalerate	Stuffed peppers	3	0.005	0.003	0.007
Fenvalerate	Raw apricot	2	0.03	0.024	0.036
Fenvalerate	Strained peaches/junior	1	0.011	0.011	0.011
Fenvalerate	Red grapes	1	0.006	0.006	0.006
Fenvalerate	Raw cherries	1	0.11	0.11	0.11
Fenvalerate	Collards	12	0.1188	0.015	0.373
Fenvalerate	Raw tomatoes	4	0.0418	0.004	0.134
Fenvalerate	Green beans	2	0.017	0.015	0.019
Fenvalerate	Okra	1	0.032	0.032	0.032
Fenvalerate	Stuffed peppers	1	0.004	0.004	0.004
Fenvalerate	Tacos	1	0.002	0.002	0.002

Table 6-3. Levels of Pyrethroids Detected in Foods

Pyrethroid	Food item	n	Mean (ppm)	Minimum (ppm)	Maximum (ppm)
Permethrin (cis)	Baked ham	1	0.001	0.001	0.001
Permethrin (trans)	Baked ham	1	0.001	0.001	0.001
Permethrin (cis)	Fried eggs	1	0.001	0.001	0.001
Permethrin (trans)	Fried eggs	1	0.0006	0.0006	0.0006
Permethrin (cis)	Dry roasted peanuts	1	0.006	0.006	0.006
Permethrin (trans)	Dry roasted peanuts	1	0.009	0.009	0.009
Permethrin (cis)	Popcorn	1	0.007	0.007	0.007
Permethrin (trans)	Popcorn	1	0.007	0.007	0.007
Permethrin (cis)	Rye bread	2	0.0099	0.0008	0.019
Permethrin (trans)	Rye bread	2	0.0109	0.0007	0.021
Permethrin (cis)	Raw peaches	3	0.0107	0.006	0.018
Permethrin (trans)	Raw peaches	3	0.014	0.006	0.027
Permethrin (cis)	Raw cantaloupe	2	0.045	0.004	0.005
Permethrin (cis)	Raw cherries	1	0.022	0.022	0.022
Permethrin (trans)	Raw cherries	1	0.022	0.022	0.022
Permethrin (cis)	Dried prunes	1	0.002	0.002	0.002
Permethrin (trans)	Dried prunes	1	0.002	0.002	0.002
Permethrin (cis)	Spinach	22	0.6283	0.003	2.31
Permethrin (trans)	Spinach	22	0.6803	0.002	2.74
Permethrin (cis)	Collards	22	0.3331	0.002	1.33
Permethrin (trans)	Collards	22	0.285	0.002	0.853
Permethrin (cis)	Iceberg lettuce	5	0.0104	0.0009	0.036
Permethrin (trans)	Iceberg lettuce	5	0.009	0.0009	0.034
Permethrin (cis)	Canned sauerkraut	1	0.0004	0.0004	0.0004
Permethrin (trans)	Canned sauerkraut	1	0.0005	0.0005	0.0005
Permethrin (cis)	Broccoli	10	0.0047	0.001	0.014
Permethrin (trans)	Broccoli	10	0.0037	0.0007	0.009
Permethrin (cis)	Raw celery	22	0.0113	0.001	0.031
Permethrin (trans)	Raw celery	22	0.0093	0.001	0.023

Table 6-3. Levels of Pyrethroids Detected in Foods

Pyrethroid	Food item	n	Mean (ppm)	Minimum (ppm)	Maximum (ppm)
Permethrin (cis)	Asparagus	2	0.0862	0.0003	0.172
Permethrin (trans)	Asparagus	2	0.1087	0.0003	0.217
Permethrin (cis)	Cauliflower	1	0.004	0.004	0.004
Permethrin (trans)	Cauliflower	1	0.002	0.002	0.002
Permethrin (cis)	Raw tomato	16	0.0072	0.0006	0.015
Permethrin (trans)	Raw tomato	16	0.0072	0.0005	0.015
Permethrin (cis)	Green beans	1	0.005	0.005	0.005
Permethrin (trans)	Green beans	1	0.003	0.003	0.003
Permethrin (cis)	Green pepper	11	0.0332	0.005	0.081
Permethrin (trans)	Green pepper	11	0.0411	0.006	0.079
Permethrin (cis)	Raw raddish	1	0.001	0.001	0.001
Permethrin (trans)	Raw raddish	1	0.0005	0.0005	0.0005
Permethrin (cis)	Meatloaf	1	0.0006	0.0005	0.0006
Permethrin (trans)	Meatloaf	1	0.0006	0.0005	0.0006
Permethrin (cis)	Butter	1	0.002	0.002	0.002
Permethrin (trans)	Butter	1	0.003	0.003	0.003
Permethrin (cis)	Half & Half cream	1	0.0003	0.0003	0.0003
Permethrin (trans)	Half & Half cream	1	0.0005	0.0005	0.0005
Permethrin (cis)	Catsup	1	0.0009	0.0009	0.0009
Permethrin (trans)	Catsup	1	0.0007	0.0007	0.0007
Permethrin (cis)	Pumpkin pie	7	0.0024	0.0006	0.006
Permethrin (trans)	Pumpkin pie	7	0.0031	0.001	0.008
Permethrin (cis)	Chicken	1	0.001	0.001	0.001
Permethrin (trans)	Chicken	1	0.0008	0.0008	0.0008
Permethrin (cis)	Vegetables and chicken	1	0.001	0.001	0.001
Permethrin (trans)	Vegetables and chicken	1	0.001	0.001	0.001
Permethrin (cis)	Strained green beans/junior	2	0.0035	0.002	0.005
Permethrin (trans)	Strained green beans/junior	2	0.0035	0.002	0.005
Permethrin (cis)	Creamed spinach/junior	8	0.0372	0.0006	0.138

Table 6-3. Levels of Pyrethroids Detected in Foods

Pyrethroid	Food item	n	Mean (ppm)	Minimum (ppm)	Maximum (ppm)
Permethrin (trans)	Creamed spinach/junior	8	0.0338	0.0004	0.12
Permethrin (cis)	Strained peaches/junior	14	0.0185	0.0006	0.078
Permethrin (trans)	Strained peaches/junior	14	0.022	0.0007	0.099
Permethrin (cis)	Strained pears/junior	3	0.0013	0.0008	0.002
Permethrin (trans)	Strained pears/junior	3	0.0009	0.0008	0.001
Permethrin (cis)	Fruit dessert/junior	17	0.0045	0.0009	0.013
Permethrin (trans)	Fruit dessert/junior	17	0.0057	0.0006	0.019
Permethrin (cis)	Veal cutlet	1	0.002	0.002	0.002
Permethrin (trans)	Veal cutlet	1	0.002	0.002	0.002
Permethrin (cis)	Wheat bread	1	0.0009	0.0009	0.0009
Permethrin (trans)	Wheat bread	1	0.0009	0.0009	0.0009
Permethrin (cis)	Canned peaches	1	0.0004	0.0004	0.0004
Permethrin (trans)	Canned peaches	1	0.0005	0.0005	0.0005
Permethrin (cis)	Canned tomatoes	3	0.0015	0.0004	0.002
Permethrin (trans)	Canned tomatoes	3	0.0016	0.0007	0.002
Permethrin (cis)	Brussel sprouts	12	0.0154	0.0004	0.127
Permethrin (trans)	Brussel sprouts	12	0.0124	0.0003	0.1
Permethrin (cis)	Mushrooms	6	0.0285	0.0003	0.159
Permethrin (trans)	Mushrooms	6	0.0221	0.0002	0.125
Permethrin (cis)	Turnips	1	0.001	0.001	0.001
Permethrin (trans)	Turnips	1	0.001	0.001	0.001
Permethrin (cis)	Okra	1	0.002	0.002	0.002
Permethrin (trans)	Okra	1	0.002	0.002	0.002
Permethrin (cis)	Beef stroganoff	1	0.018	0.018	0.018
Permethrin (trans)	Beef stroganoff	1	0.01	0.01	0.01
Permethrin (cis)	Stuffed peppers	9	0.0138	0.0005	0.074
Permethrin (trans)	Stuffed peppers	9	0.0171	0.0007	0.093
Permethrin (cis)	Tuna casserole	6	0.0014	0.0008	0.002
Permethrin (trans)	Tuna caracole	6	0.0012	0.0005	0.003

Table 6-3. Levels of Pyrethroids Detected in Foods

Pyrethroid	Food item	n	Mean (ppm)	Minimum (ppm)	Maximum (ppm)
Permethrin (cis)	Quarter pound cheeseburger	1	0.005	0.005	0.005
Permethrin (trans)	Quarter pound cheeseburger	1	0.001	0.001	0.001
Permethrin (cis)	Tacos	3	0.0015	0.0004	0.003
Permethrin (trans)	Tacos	3	0.0018	0.0005	0.004
Permethrin (cis)	Pizza	2	0.0006	0.0004	0.0007
Permethrin (trans)	Pizza	2	0.0006	0.0003	0.0008
Permethrin (cis)	Beef chow mein	6	0.0016	0.0006	0.003
Permethrin (trans)	Beef chow mein	6	0.001	0.0006	0.002
Permethrin (cis)	Split peas with vegetables and ham	1	0.0008	0.0008	0.0008
Permethrin (trans)	Split peas with vegetables and ham	1	0.0009	0.0009	0.0009
Permethrin (cis)	Strained squash/junior	2	0.0009	0.0008	0.0009
Permethrin (trans)	Strained squash/junior	2	0.0009	0.0008	0.0009

n = number of detections

Source: FDA 2000c

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population is exposed to pyrethrins and pyrethroids primarily from food sources, especially fruits and vegetables. The average daily intake (AVDI) of permethrin per unit of body weight (ng/kg-body weight-per day) in eight population groups was estimated using the FDA's monitoring program for chemical contaminants in the U.S. food supply. The data were obtained from the FDA Total Diet Studies conducted in 1982–1984 (Gunderson 1988), 1984–1986 (Gunderson 1995a), and 1986–1991 (Gunderson 1995b) and are summarized in Table 6-4. These data can be compared to the United Nations' Food and Agriculture Organization (FAO) and the World Health Organization (WHO) acceptable daily intake (ADI) value for technical-grade permethrin of 50,000 ng/kg-body weight per day (Gunderson 1995b). The ADI of a chemical is defined as the maximum daily intake, which, during a lifetime, appears to be without appreciable risk. These values can be used to derive a rough estimate for the AVDI for all pyrethrins and pyrethroids because permethrin is the pyrethroid found most often in foods (see Table 6-3).

Many household products used to control insects, such as aerosol bombs, spray insecticides, and pet shampoos, contain pyrethrins and pyrethroids, and therefore, dermal and inhalation exposures are possible. Because of the low mobility of these compounds in soil surfaces, pyrethrins and pyrethroids are rarely detected at elevated levels in drinking water or groundwater, with the exception of shallow wells near agricultural areas.

Occupational exposure to pyrethrins and pyrethroids will occur by inhalation and dermal contact with these compounds at workplaces where they are produced or used. The National Institute of Occupational Safety and Health (NIOSH) has conducted National Occupational Exposure Surveys (NOES) for pyrethrum and selected pyrethroids (NIOSH 1989). The NOES data do not include farm workers who are likely to be exposed to these compounds. Therefore, the estimated occupational exposures reported are likely to be greatly underestimated. Furthermore, these surveys were conducted prior to the development of many of the more recent pyrethroids and no current surveys exist. NIOSH (NOES 1981–1983) has statistically estimated that 11,296 total workers (1,537 of these are females) are exposed to pyrethrum in the United States (NIOSH 1989). Similarly, NIOSH has statistically estimated that 9,244 workers (1,758 of these are female) are potentially exposed to tetramethrin in the United States, and 27,596 workers (3,998 of these are female) are potentially exposed to resmethrin in the United States (NIOSH 1989). The NOES database does not contain information on the frequency, level, or duration of

Table 6-4. Average Daily Intake (AVDI, ng/kg/day) of Permethrin in Eight Population Groups

Date	Infants (6–11 months)	Toddlers (2 years)	14–16-year-old females	14–16-year-old males	25–30-year-old females	25–30-year-old males	60–65-year-old females	60–65-year-old males
1982–1984[a]	1.2	5.6	3.3	3.0	5.0	4.1	6.5	5.4
1984–1986[b]	89	25	10.7	14.9	15.1	13.7	24.2	22.4
1986–1991[c]	46.5	70.7	35.7	41.5	56.5	46.0	58.6	59.2

[a] Gunderson 1988
[b] Gunderson 1995a
[c] Gunderson 1995b

the exposure of workers to any of the chemicals listed therein. They are surveys that only provide estimates of workers potentially exposed to the chemicals.

The concentration of 3-phenoxybenzoic acid (3-PBA), a urinary metabolite of permethrin, was measured in the urine of an agricultural worker in Japan exposed to this pyrethroid during its application to cabbage plants (Asakawa et al. 1996). The concentration of 3-PBA was 2.9 ng/mL (6 hours postapplication), 5.1 ng/mL (the morning after application), and 1.4 ng/mL (3 days postapplication) (Asakawa et al. 1996). Even though the worker was covered by protective clothing, it was determined that permethrin permeated the worker's clothing and led to significant dermal exposure, particularly on the arms and legs (Asakawa et al. 1996). In a study of 50 Chinese workers applying deltamethrin and fenvalerate onto cotton fields, it was determined that dermal exposure represented the main route of exposure for the workers. Inhalation exposure rates were determined to be on the order of μg/hour, while dermal exposure was on the order of mg/hour (Zhang et al. 1991). Dermal exposure to deltamethrin for a pilot applying the insecticide on crops while flying an ultra-light aircraft was estimated as 10.8 μg/hour (Yoshida et al. 1990). A ground-based flagman on duty during the aerial spraying received an estimated dermal exposure of 25.4 μg/hour and dermal exposure to workers manually spraying deltamethrin was 2,800–65,400 μg/hour (Yoshida et al. 1990). The 1,000-fold exposure difference between hand-held applicators and aerial applicators was due, in part, to work practices of the workers. Dermal exposures on different regions of the bodies of 6 pesticide applicators who sprayed cypermethrin in tea plantations in China were measured (Wan 1990). Exposures (in μg/100 cm^2) were as follows: face: 0.06–0.72; chest: 0.11–2.06; abdomen: 0.09–2.68; thigh: 0.41–17.3; and ankle: 0.15–32.6. Total dermal exposures based upon spray amounts were 186–1,140 mg/kg for nonhand areas and 46.1 mg/kg for hands only (Wan 1990). Dermal exposure to permethrin was shown to be far greater than inhalation exposure for two applicators involved in the spraying of this pyrethroid onto tomatoes in greenhouses (Adamis et al. 1985). The estimated respiratory exposure rate for these workers was 0.004 mg/hour and the dermal exposure rate was 3.8 mg/hour (Adamis et al. 1985). However, based upon the findings of animal studies, the absorption of pyrethroids is likely to be higher via oral and inhalation pathways when compared to dermal absorption (Eadsforth et al. 1988; van der Rhee et al. 1989; Woollen et al. 1992). Estimates of pyrethroid absorption in humans following dermal application range from about 0.3 to 1.8% of the administered dose (see Section 3.4).

6.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in 3.7 Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (NRC 1993).

Children are exposed to pyrethrins and pyrethroids by similar routes that affect adults. Ingestion of foods is the most important exposure pathway for children. The AVDI of permethrin has been reported as 46.5 ng/kg-body weight/day for 6–11-month-old infants and 70.7 ng/kg-body weight/day for 2-year-old toddlers (Gunderson 1995b). No measurements have been made of these compounds in amniotic fluid, meconium, cord blood, neonatal blood, or any other tissues that may indicate prenatal exposure. No data have been reported on the levels of pyrethrins or pyrethroids in breast milk.

The tendency of young children to ingest soil, either intentionally through pica or unintentionally through hand-to-mouth activity, is well documented. These behavioral traits can result in ingestion of pyrethrins and pyrethroids present in soil and dust. Since these compounds are adsorbed strongly to soils, they may not be in a highly bioavailable form. Young children often play on the ground or on carpets and this will increase the likelihood of dermal exposure and inhalation of contaminated particles from soil, household dust and treated surfaces. The transfer of allethrin residues from a carpeted floor to human subjects wearing dosimeter clothing was studied (Ross et al. 1990). For gloves, socks, shirts, and tights of subjects performing standardized aerobic exercises, the transfer coefficient ranged from 2.8 to 34.3 μg allethrin/cm^2 clothing for a period of up to 12.5 hours after applying allethrin (via foggers) to the carpet. The transfer rates decreased with time after application (Ross et al. 1990). Pyrethrins and pyrethroids are also frequently used in products such as pet shampoos or sprays, and since children often spend a great deal of time playing with pets, this can increase childhood exposure. Pyrethrins and certain pyrethroids have been employed in head lice treatment products, which are often used on children. Very little data were located regarding the concentrations of pyrethroids in milk and dairy samples. No pyrethroids were detected in any milk or dairy samples from the FDA Market Basket Surveys compiled from the 1991 to 1999 data (FDA 2000c). However, cypermethrin was detected in the milk from cows wearing ear tags impregnated with cypermethrin to control certain insects (Braun et al. 1985). Flumethrin, deltamethrin, cypermethrin, and cyhalothrin were detected in the milk of cows after single dermal applications (Bissacot and Vassilieff 1997a). Children may be exposed to pyrethrins and pyrethroids from the clothing of parents who work as pesticide applicators. Asakawa et al. (1996) documented that permethrin adhered to a worker's clothing and different parts of the body following the application of this insecticide onto a cabbage field. Similar findings were obtained for cotton sprayers using deltamethrin and fenvalerate (Zhang et al. 1991). Washing the affected clothing does not necessarily assure that all of the pyrethroids will be removed from the contaminated garments. Fabrics that simulated the clothing worn by workers applying cypermethrin insecticides were found to contain 1.7–2.3 $\mu g/cm^2$ before laundering; after laundering, levels of 0.3–1.1 ng/cm^2 remained in the fabric (Laughlin et al. 1991). A study was conducted to determine the ability of laundry practices used by farm families to remove pesticides from clothing (Rigakis et al. 1987). After one wash, 2–18% of initial deltamethrin remained on fabrics, and after two washes, 1–10% of initial deltamethrin remained on fabrics (Rigakis et al. 1987). Pretreating the fabric with a prewash spot removal product especially formulated to assist in the removal of oily stains resulted in the lowest recoveries. Cotton strips were coated with deltamethrin and then rinsed in deionized water for 1 hour (Hussain and Perschke 1991). After four rinses, only 37.7% of the initial deltamethrin was removed from the cotton. Impregnating the cotton with various paraffin wax and oils (corn, linseed, silicone) before coating with deltamethrin resulted in even lower percentages removed when washed (9.9–29.2% removal).

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Aside from agricultural workers or insect control applicators, populations with potentially high exposures to pyrethrins or pyrethroids are small. Workers involved in the manufacturing and production of these insecticides are likely to be exposed to higher levels than the general population. Veterinarian professionals or pet groomers who frequently apply pyrethrin- and pyrethroid-containing shampoos or flea applications to animals may also be exposed to high levels of these compounds through dermal routes. Persons residing near farms or orchards may be subject to spray drift following application of these insecticides onto crops. Humans who use shampoos or sprays that contain pyrethrins or pyrethroids for their pets are likely to be exposed to higher levels of these compounds than persons without pets.

Home gardeners who use pyrethroids and pyrethrins for insect control either in the garden or within the household itself may be exposed to high levels. Diet is also a key factor in relative human exposure level to pyrethrins and pyrethroids. As shown in Table 6-3, these compounds are frequently detected at varying levels in fruits and vegetables.

Permethrin is part of the United States Department Of Defense (DOD) Insect Repellent System and was issued in the Persian Gulf War to military personnel as a ready to use insect repellent for clothing application. It is also labeled for use on battle dress clothing and bed netting (Cecchine et al. 2000). Phenothrin was also used for spraying on bed netting and inside of aircrafts to prevent transport of insects. Due to an absence of sampling data and information about pesticide application rates, individual exposures were reconstructed by means of interviews with service personnel. The DOD reported that approximately 44 and 28% of all service personal in the Gulf used permethrin and phenothrin sprays, respectively, and that the guidelines for their recommended use were not always strictly adhered to (DOD 2001). This may have led to excessive exposures to these insecticides by some members of the military serving in the Persian Gulf.

6.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of pyrethrins and pyrethroids are available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of pyrethrins and pyrethroids.

The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

6.8.1 Identification of Data Needs

Physical and Chemical Properties. As illustrated in Tables 4-4 and 4-5, the relevant physical and chemical properties of pyrethrins and the pyrethroids that are used in the United States are not entirely known. There are several pyrethroids that have been developed, and adequate data may not be available for all of them (Mueller-Beilschmidt 1990). Furthermore, inert ingredients used in formulated pesticide products are usually not disclosed. This makes a thorough evaluation of the final commercial product challenging. Complete disclosure of all the ingredients used in a formulated product would aid in the evaluation of both physical and toxicological properties of the pesticide.

Production, Import/Export, Use, Release, and Disposal. Knowledge of a chemical's production volume is important because it may correlate with environmental contamination and human exposure. If a chemical's production volume is high, then there is an increased probability of general population exposure via consumer products and environmental sources, such as air, drinking water, and food.

The TRI99 (2001), which became available in 2001, has been used in this profile. The only pyrethroids that are on the list are allethrin, bifenthrin, cyfluthrin, cyhalothrin, fenpropathrin, fluvalinate, permethrin, phenothrin, resmethrin, and tetramethrin (TRI99 2001). Furthermore, data have only been reported for bifenthrin, cyfluthrin, permethrin, resmethrin, and tetramethrin. More detailed site- and medium-specific (e.g., air, water, or soil) release data for more pyrethroids are necessary. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. TRI, which contains this information for 1999, became available in 2001. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Environmental Fate. Information is available to permit assessment of the environmental fate and transport of the pyrethrins and pyrethroids in air (Chen and Casida 1969; Chen et al. 1984; HSDB 2001; Samsonov and Makarov 1996; Ueda et al. 1974), water (Maguire 1990; Rawn et al. 1982; Schimmel et al. 1983; USDA 2001a), and soil (Chapman et al. 1981; Hill 1983; Khan et al. 1988; Smith et al. 1995; USDA 2001a). Most of these compounds are rapidly degraded in the air by photolysis or through the reaction with oxidants such as hydroxyl radicals, ozone, or nitrate radicals found in the atmosphere. Many of the recently developed pyrethroids such as cyhalothrin are more stable towards sunlight than the early light sensitive pyrethroids like allethrin and resmethrin. Volatilization from water surfaces may be an important fate process for pyrethrins and pyrethroids with relatively large Henry's law constants, but adsorption to suspended solids and sediments will attenuate this process. Photolysis in sunlit surface waters has been demonstrated for several pyrethroids (Maguire 1990; Rawn et al. 1982; Schimmel et al. 1983). Hydrolysis is also an important environmental fate process in water or moist soil under alkaline conditions (Chapman and Cole 1982; USDA 2001a). Biodegradation occurs in water, soil, and sediment at varying rates (Cotham and Bidleman 1989; Hill 1983; Schimmel et al. 1983; Smith et al. 1995; USDA 2001a). Photolysis and volatilization of these compounds can occur on soil and plant surfaces (Hill and Johnson 1987; Takahashi et al. 1985a). These compounds are not expected to leach extensively since they have very little mobility in soils (USDA 2001a).

While it can be reasonably concluded that pyrethrins will biodegrade in the environment based upon their chemical structure, there are no specific biodegradation studies of the six pyrethrins. Furthermore, there are several synthetic pyrethroids for which experimental data regarding their biodegradation, bioconcentration, photolysis, adsorption, and hydrolysis are not available. Studies on these pyrethroids are warranted.

Bioavailability from Environmental Media. The bioavailability of pyrethrins and pyrethroids from contaminated air, water, soil, or plant material in the environment has not been adequately studied. ^{14}C-labeled deltamethrin was used to treat wheat grains that were ultimately fed to rats (Khan et al. 1990). The ^{14}C residues were excreted in the urine and feces of the rats and trace amounts were also present in the lungs and kidneys, which suggests that the bound deltamethrin residues in the wheat were bioavailable (Khan et al. 1990). A similar experiment was performed using deltamethrin ^{14}C labeled at either the methyl or benzylic position applied to bean plants (Khan et al. 1986). Four days after feeding rats the contaminated material, 60% (methyl ^{14}C labeled) and 53% (benzylic ^{14}C labeled) of the dose was excreted in the feces, while 31% (methyl ^{14}C labeled) and 20% (benzylic ^{14}C labeled) of the dose was excreted in the urine. No radioactivity was detected in the liver, kidney, brain, or lung tissue of the sacrificed rats. Workers applying pyrethroids in the field have a much greater dermal exposure rate when compared to inhalation exposure (Adamis et al. 1985; Wan 1990; Yoshida et al. 1990; Zhang et al. 1991), but the percentage of pyrethroid absorbed dermally is less than oral and inhalation absorption (Eadsforth et al. 1988; van der Rhee et al. 1989; Woollen et al. 1992). Since these compounds adsorb strongly to soils, bioavailability from soil may be limited, but absorption and bioavailability studies of these compounds from soils are lacking. Studies are needed on the bioavailability of these compounds from actual environmental media and on differences in bioavailability for the various pyrethrins and pyrethroids.

Food Chain Bioaccumulation. Bioconcentration occurs in aquatic organisms (Freitag et al. 1985; Haitzer et al. 1998; Schimmel et al. 1983). There is no evidence to indicate that bioaccumulation occurs in aquatic or terrestrial species, but studies are needed to determine if pyrethrins and pyrethroids bioaccumulate up the food chain.

Exposure Levels in Environmental Media. Atmospheric concentrations of pyrethrins or pyrethroids are usually on the order of $\mu g/m^3$ immediately after their application (Eitzer 1991; Siebers and Mattusch 1996), but the levels decrease with time because these compounds undergo rapid degradation in the atmosphere. These compounds are infrequently detected in groundwater and drinking water in the United States because of their strong adsorption to soils and relatively rapid rate of degradation. Pyrethrins and pyrethroids are found in soils following their application, but their levels decrease with time. The average concentration of permethrin in soils collected from 48 agrochemical facilities located throughout the state of Illinois was 190 µg/kg (Krapac et al. 1995). More data regarding the levels of pyrethrins and pyrethroids in water and soil surfaces are needed in order to produce better estimates of the potential for human exposure to these compounds. Foods, especially fruits and vegetables, have been shown to contain pyrethroids at varying levels (Table 6-3). Continued monitoring data of these compounds in foods are necessary since ingestion of food sources is the most likely route of widespread human exposure.

Exposure Levels in Humans. The general population is exposed to pyrethrins and pyrethroids primarily through the ingestion of food sources. The AVDI of permethrin, the most frequently used pyrethroid in the United States, has been estimated for eight different population groups (Gunderson 1988, 1995a, 1995b). Additional data regarding the AVDI for other pyrethroids and pyrethrins would be useful in assessing total exposure for the U.S. population. The use of household insecticides containing these compounds can also lead to dermal and inhalation exposure. Workers employed in the agricultural industry, veterinary industry, or pet grooming business may be occupationally exposed to high levels of these compounds. Dermal exposure has been shown to be greater than inhalation exposure for applicators involved in the spraying of pyrethroids (Adamis et al. 1985; Wan 1990), but dermal absorption appears to be lower than the amount absorbed from the other routes. While body burden studies were located for persons occupationally exposed (Asakawa et al. 1996; Wan 1990), body burden studies are needed for the general population of the United States.

Exposures of Children. Estimates regarding the AVDI of permethrin for children are available (Gunderson 1988, 1995a, 1995b). Additional data regarding the AVDI for other pyrethroids and pyrethrins would be useful to assess childhood exposure more thoroughly. Body burden studies of children are also necessary. Since children may be exposed to these compounds from pica, bioavailability studies from soils would be useful for a wide array of pyrethrins and pyrethroids.

Child health data needs relating to susceptibility are discussed in 3.12.2 Identification of Data Needs: Children's Susceptibility.

Exposure Registries. No exposure registries for pyrethrins and pyrethroids were located. These substances are not currently among the compounds for which a subregistry has been established in the National Exposure Registry. The substances will be considered in the future when chemical selection is made for subregistries to be established. The information amassed in the National Exposure Registry facilitates epidemiological research needed to assess adverse health outcomes that may be related to exposure to pyrethrins and pyrethroids.

The development of a registry of exposures would provide a useful reference tool for monitoring exposure levels and frequencies over time. Such a registry would allow an assessment of the variations in exposure levels from various sources. Also it could be used to assess the effect of geographical, seasonal, or regulatory actions on the level of exposure from a certain source. These assessments, in turn, would provide a better understanding of the needs for research or data acquisition based on the current exposure levels.

6.8.2 Ongoing Studies

The Federal Research Programs In Progress (FEDRIP 2001), Current Research Information System (CRIS/USDA 2001), and Computer Retrieval of Information on Scientific Projects (CRISP 2001) databases indicate that several projects are ongoing that may fill some existing data gaps. Symbiotech Inc., located in Wallingford, Connecticut, is investigating a topical preparation of permethrin intended for use on humans as an insect repellent (FEDRIP 2001). Researchers at the University of Arkansas (Dr. Meisch and Dr. Bernhardt) are investigating the efficacy and environmental effects of various pyrethroids for mosquito control in riceland systems (CRIS/USDA 2001). Dr. Epstein from the University of

California Davis, is developing software based on the California Department of Pesticide Regulation's Pesticide Use Reports to document trends in fungicide and insecticide use on grapes and almonds, respectively (CRIS/USDA 2001). Dr. Hammock from the University of California Davis is attempting to develop and validate single compound, as well as class selective immunoassays for urinary metabolites of hazardous compounds (including pyrethroids) for use as biomarkers of internal exposure to these compounds (CRISP 2001).