

## 6. POTENTIAL FOR HUMAN EXPOSURE

### 6.1 OVERVIEW

Malathion has been identified in at least 21 of the 1,623 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2003). However, the number of sites evaluated for malathion is not known. The frequency of these sites can be seen in Figure 6-1. All of the 1,623 sites are located within the United States; none of the sites are located in the Commonwealth of Puerto Rico.

Malathion is an insecticide used for agricultural and nonagricultural purposes that is released to the environment primarily through spraying on agricultural crops and at agricultural sites, spraying for home and garden use, and spraying for public health use in both urban/residential and nonresidential areas; the insecticide is also released to the environment using fogging equipment. Once malathion is introduced into the environment, it is degraded by atmospheric photooxidation, hydrolysis, or biodegradation mediated by microorganisms found in most sediment, soils, and water. The oxon degradate of malathion, malaoxon, which is more toxic than malathion, is formed from the oxidation of malathion and may also be present as an impurity in the parent compound. Malathion and malaoxon can be transported from the site of application by precipitation, fog, and wind to other areas. Malathion is moderately mobile to very highly mobile in soils, creating the potential for it to move through the soil profile and into groundwater. However, because degradation of malathion occurs rapidly in the environment, the potential for malathion movement into groundwater is generally not significant and leaching of the chemical into groundwater is usually not observed. Volatilization of malathion from ground surfaces following aerial applications has been observed. Data from limited studies suggest that bioconcentration of malathion does not occur to a significant extent in most aquatic organisms tested because it is rapidly metabolized. Malathion is not widely dispersed or persistent in the environment, but is detected frequently in foods. Residue amounts of malathion have been detected in air, water, soil, fish, and agricultural crops consumed as food.

The general population is not likely to be exposed to large amounts of malathion. Some exposure to residues of malathion is possible, however, as many studies show that malathion has been detected in foods and atmosphere samples. Populations living within or very near areas of heavy malathion use would have an increased risk of exposure to relatively larger amounts of malathion through dermal contact with contaminated plants, by inhalation of the mist formed from the applied insecticide, or by



## 6. POTENTIAL FOR HUMAN EXPOSURE

ingestion of water or food-borne residues. Also at increased risk of exposure are persons utilizing malathion for extensive home and garden use, particularly if they consume contaminated, unwashed backyard produce. Those likely to receive the highest levels of exposure are those who are involved in the production, formulation, handling, and application of malathion, as well as farm workers who enter treated fields prior to the passage of the appropriate restricted entry intervals. Dermal contact appears to be the major route of exposure, while ingestion may also be an important route of exposure. Inhalation has not been shown to be a significant route of exposure to malathion.

### 6.2 RELEASES TO THE ENVIRONMENT

Malathion has been released to the environment mainly as a result of its use as an insecticide on food and feed crops, noncrop agricultural use, home and garden use, and public health use (for medfly and mosquito control). It is also released as a result of USDA special program usage such as the USDA Boll Weevil Eradication Program, which accounts for approximately 90% of malathion agricultural crop usage (EPA 2000a). Additionally, malathion is used as a pharmaceutical for humans. It is applied in the environment mainly by aerial, ground spraying, or fogging equipment, but is also used in bait type formulations (i.e., applied to food baits). The annual use of malathion in 1994 was reported to be 3,377,681 pounds, of which 782,434 pounds were used in the state of California (Wilson et al. 1997). There are no known natural sources of the compound. Malathion has been identified in at least 21 of the 1,623 hazardous waste sites on the NPL (HazDat 2003).

According to recent Toxics Release Inventory (TRI) data, malathion was discharged to air from four processing sites and to water from one processing site in the United States in 2000; no releases to soil were reported for that year (TRI00 2002). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

#### 6.2.1 Air

As a result of its use as an insecticide on cotton, sod/turf, ornamentals, berries, fruit trees, vegetables, and other crops; its use in regional pest eradication programs, including public health use for medfly quarantine and mosquito abatement; its noncrop agricultural site use; and its outdoor home and garden use, malathion is released directly to the atmosphere during application. It is applied primarily by

## 6. POTENTIAL FOR HUMAN EXPOSURE

spraying from aircraft or from ground spray or fogging equipment (EPA 2000a). Aerial application of malathion to agricultural fields and to residential or other target areas releases the insecticide to the air.

Following repeated aerial applications of malathion, at a target rate of 23.8 mg/m<sup>2</sup>, to urban/residential areas (1,500 km<sup>2</sup>) of southern California between August 1989 and July 1990 to eradicate Mediterranean fruit flies (Medflies), the California Department of Food and Agriculture (CDFA) Environmental Monitoring Branch measured the mass deposition, air concentrations, and selected water concentrations of malathion and its primary oxidation product, malaoxon (Bradman et al. 1994). The mean mass deposition of the malathion (originally released to the air; for the first application only) at a target rate of 23.8 mg/m<sup>2</sup> was 22.1 mg/m<sup>2</sup>, with a range of 1.7–53.7 mg/m<sup>2</sup> (Bradman et al. 1994). Following the release to air, the maximum mean concentrations (averaged for three sites) of malathion and malaoxon in the air were 61.6 ng/m<sup>3</sup> at 24 hours and 48.1 ng/m<sup>3</sup> at 24–48 hours, respectively (Brown et al. 1993b).

Malathion may also be released into the air as a result of volatilization from crop surfaces. As a result of summertime agricultural use in the Central Valley in California, malathion was released to the air by volatilization and was transported to higher elevation regions of the Sierra Nevada Mountains (LeNoir et al. 1999). In a study of the air, rain, and surface water associated with a subestuary of the Chesapeake Bay estuarine drainage system (in the Patuxent River watershed), which includes 57,000 km<sup>2</sup> of agricultural cropping areas, malathion was present in 30% of the air samples and 50% of the rain samples (used to determine wet deposition flux) collected in the spring and summer of 1995 (Harman-Fetcho et al. 2000).

No data were found on releases to the atmosphere from production facilities and disposal sites. Based on a measured Henry's law constant of 4.89x10<sup>-9</sup> atm/m<sup>3</sup> mol (Fendinger and Glotfelty 1990) and a measured vapor pressure of 3.38x10<sup>-6</sup> mm Hg (USDA Pesticide Property Database), it is considered unlikely that malathion will be released to the air to any significant extent as a result of volatilization from either moist or dry soil surfaces or water surfaces at disposal sites.

Malathion was detected in air at 1 of the 1,623 current or former NPL sites where malathion has been identified in some environmental medium (HazDat 2003).

The most recent TRI data indicate that 11 sites in the United States processed malathion in 2000 (TRI00 2002). The total of reported releases to air was 3,094 pounds, representing 99.7% of all environmental

## 6. POTENTIAL FOR HUMAN EXPOSURE

releases (Table 6-1). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

### 6.2.2 Water

Malathion can potentially be released to surface waters by direct application; storm runoff from sprayed fields or urban/residential areas; atmospheric deposition following aerial application (wet deposition from rain and fog water); waste water releases from formulation, manufacturing, or processing facilities; and spills.

Malathion has been released to shoreline beaches and surface waters in adjacent coastal marshes on the eastern coast of central Florida for mosquito control using aerial spraying and truck-mounted (ultra-low volume; ULV) equipment (Clark et al. 1993).

Malathion has been detected in three rivers, which are the three largest tributaries to the Chesapeake Bay (Foster and Lippa 1996). Malathion was collected in 6–16% of the water samples collected from the Susquehanna, Potomac, and James Rivers in 1992–1993; mean aqueous concentrations of malathion in the three rivers were 6, 12, and 7 ng/L, respectively. Annual loads of malathion from the three respective tributaries to the Chesapeake Bay were determined to be 8–86, 3–25, and 3–18 kg/year, respectively (Foster and Lippa 1996).

Malathion has been released to surface waters as a result of wet deposition following volatilization from crop surfaces and transport through the atmosphere. Reportedly as a result of summertime agricultural use in the Central Valley in California, and following volatilization from crop surfaces and transport through the atmosphere, malathion was released to surface waters by wet deposition in higher elevation regions of the Sierra Nevada Mountains; malathion was not detected in any of the dry deposition samples (LeNoir et al. 1999). Malathion was detected in the surface waters transecting the Central Valley to the Sierra Nevada Mountains at aqueous concentrations of 65–83 ng/L; the compound was not detected in surface water samples collected from the two highest (of eight) elevations studied. In a study of the air, rain, and surface water associated with a sub-estuary of the Chesapeake Bay estuarine drainage system (in the Patuxent River watershed), which includes 57,000 km<sup>2</sup> of agricultural cropping areas, the total wet deposition flux of malathion in the spring and summer of 1995 was determined to be 5,200 ng/m<sup>2</sup> (in the 200 mm of rain that fell during the study period; Harman-Fetcho et al. 2000). The wet deposition flux of

## 6. POTENTIAL FOR HUMAN EXPOSURE

**Table 6-1. Releases to the Environment from Facilities that Produce, Process, or Use Malathion**

Reported amounts released in pounds per year <sup>a</sup>								
State <sup>b</sup>	Number of facilities	Air <sup>c</sup>	Water	Under-ground injection	Land	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	Total on and off-site release
AR	1	1	No data	No data	No data	1	No data	1
GA	3	41	5	No data	No data	46	18	64
IA	1	539	No data	No data	No data	539	No data	539
MO	2	2,818	No data	No data	No data	2,818	No data	2,818
MS	1	250	0	No data	No data	250	No data	250
TX	3	255	5	No data	0	260	250	510
Total	11	3,904	10	No data	0	3,914	268	4,182

Source: TRI00 2002

<sup>a</sup>Data in TRI are maximum amounts released by each facility.

<sup>b</sup>Post office state abbreviations are used.

<sup>c</sup>The sum of fugitive and stack releases are included in releases to air by a given facility.

<sup>d</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>e</sup>Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW).

## 6. POTENTIAL FOR HUMAN EXPOSURE

malathion for the 24 measured rain events ranged from 8 to 1,800 ng/m<sup>2</sup>; malathion was detected in only 50% of the collected samples.

No information was found in the literature on the release of malathion to water by spillage, or on waste water releases from formulation, manufacturing, or processing facilities. In a study of pesticides in storm water runoff in the Sacramento River Basin in California, malathion was not detected; however, the limit of detection for the compound was 35 ng/L (Domagalski 1996).

Malathion has been detected in surface water at 4 of the 1,623 current or former NPL sites where malathion has been identified in some environmental medium (HazDat 2002). Malathion has been detected in groundwater at 7 of the 1,623 current or former NPL sites where malathion has been identified in some environmental medium (HazDat 2003).

The most recent TRI data indicate that 11 sites in the United States processed malathion in 2000 (TRI00 2002). The total of reported releases to water was 10 pounds, representing 0.26% of all environmental releases (Table 6-1). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

### 6.2.3 Soil

Malathion is primarily released to soils through direct deposition of spray droplets, which reach the soil surface following aerial spraying, ground spraying, and fogging applications. These releases to soil may occur following applications that are either made directly to soil (public health use in residential areas) or to crops. Releases to soil may also occur as a result of wet deposition of malathion. Approximately 12.5 million pounds of malathion are applied to agricultural crops annually in the United States, with approximately 90% of it applied through the USDA Boll Weevil Eradication Program (EPA 2000a). In 1997, over 10 millions pounds of malathion were released to areas of Texas and Alabama for this purpose (EPA 2000a). In the four counties closest to Sequoia National Park in California's Central Valley, 28,683 kg of malathion were applied to approximately 900,000 acres of harvested cropland in 1995, with the peak release period occurring in March (McConnell et al. 1998). Additionally, approximately 0.5 and 3.4 million pounds are released to soil annually through applications to both agricultural sites (e.g., roads, ditches, and near buildings) and nonagricultural sites (medfly and mosquito control, golf courses, home and garden use), respectively (EPA 2000a).

## 6. POTENTIAL FOR HUMAN EXPOSURE

Following repeated aerial applications of malathion, at a target rate of 23.8 mg/m<sup>2</sup>, to urban/residential areas (1,500 km<sup>2</sup>) of southern California between August 1989 and July 1990 to eradicate medflies, the CDFA Environmental Monitoring Branch measured the mass deposition, air concentrations, and selected water concentrations of malathion and its primary oxidation product, malaoxon (Bradman et al. 1994). Mass deposition of malathion ranged from 1,100 to 2,413 µg/ft<sup>2</sup>; mass deposition of malaoxon ranged from 2.9 to 6.0 µg/ft<sup>2</sup> (Brown et al. 1993b). Based on measured values of mass deposition, daily malathion and malaoxon residue levels in soil were estimated for a single application. Based on a mixing depth of 1 cm, soil concentrations of the parent and its oxon degradate were estimated as 1.4 and 0.01 µg/g, respectively; based on a mixing depth of 0.1 cm, the corresponding estimated concentrations in soil were 14.1 and 0.10 µg/g (Bradman et al. 1994).

Malathion may also be released to the soils by improper handling of pesticide formulations during processing or handling, including from spills or the usage of poor storage and containment practices. In a study of 49 randomly chosen agrichemical facilities located throughout Illinois, malathion was detected in soil samples at 6 of the 18 sites that handled the compound (Krapac et al. 1995). Malathion was detected in 11 of the soil samples from the six sites, at a mean concentration of 125 µg/kg (ppm) and at a concentration range of 31–690 µg/kg; the common range of detections was 22–100 µg/kg.

Malathion has been detected in soil at 11 of the 1,623 current or former NPL sites where malathion has been identified in some environmental medium (HazDat 2003). Malathion has been detected in sediment at 4 of the 1,623 current or former NPL sites where malathion has been identified in some environmental medium (HazDat 2003).

The most recent TRI data indicate that 11 sites in the United States processed malathion in 2000 (TRI00 2002); no releases to soil were reported for that year (Table 6-1). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

### 6.3 ENVIRONMENTAL FATE

The malathion released to the atmosphere can be transported back to surface water and soil by wet deposition (Harman-Fetcho et al. 2000; McConnell et al. 1998). Malathion that is released to the atmosphere can also be transformed by indirect photolysis to its oxygen analog, malaoxon, by oxidation with photochemically produced hydroxyl radicals (Howard 1991).

## 6. POTENTIAL FOR HUMAN EXPOSURE

In surface waters, malathion degrades by hydrolysis and microbially mediated biodegradation (Mulla et al. 1981). Hydrolysis is considered to be the predominant degradation process, and occurs more rapidly at alkaline pHs, while the compound is stable to hydrolysis at acidic pHs (Wolfe et al. 1975). Malathion appears to be relatively stable to direct aqueous photolysis, but may be transformed in the water by indirect photolysis. Adsorption to sediment and suspended particulate matter is not expected to be a significant factor in the fate of the compound in the environment.

In soil and sediments, the major degradation process of malathion is microbially mediated biodegradation, which occurs mainly through enzyme-catalyzed hydrolysis (Mulla et al. 1981). The predominant pathway for the biodegradation of malathion has been reported to be carboxylesterase activity (Laveglia and Dahm 1977). Malathion degrades rapidly in soil, with reported half-lives ranging from hours to approximately 1 week (Gibson and Burns 1977; Howard 1991; Konrad et al. 1969). Half-life values in soil of 3–7 days have been reported for the degradate malaoxon (Bradman et al. 1994). Based on limited data, malathion does not appear to photodegrade on soils (Chukwudebe et al. 1989; EPA 2000a). Little malathion appears to volatilize from soil (EPA 2000a) and, while malathion is moderately to highly mobile in soils (EPA 2000a), leaching of malathion through the soil and into groundwater is unlikely due to the rapid degradation of the compound in the environment.

### 6.3.1 Transport and Partitioning

Data indicate that malathion may be transported in the air following application to either agricultural or urban/residential areas (LeNoir et al. 1999; Majewski et al. 1998). Malathion may be transported in the atmosphere as a vapor or adsorbed onto particulate matter (Bossan et al. 1995). In a review paper, Mulla et al. (1981) stated that the occurrence of malathion in the atmosphere is generally localized. However, in a non-U.S. study of malathion adsorbed to fly ash (particulate matter), Bosson et al. (1995) determined that adsorbed malathion is photodegraded when exposed to irradiation of >290 nm for up to 1.5 hours, but does not degrade when adsorbed to kaolin. These study results indicate that malathion adsorbed to kaolin may be transported over long distances, while malathion adsorbed to fly ash will be rapidly photodegraded and, therefore, will not be transported far in the atmosphere (Bosson et al. 1995). Additionally, malathion has been detected in the fog of remote pristine areas, indicating that long-range transport may occur under some conditions (Rice 1996).

Transport of malathion residues in air may follow aerial applications or result from spray drift or postapplication volatilization; however, the latter source may not be significant for this compound. The

## 6. POTENTIAL FOR HUMAN EXPOSURE

Henry's law constant for malathion is  $4.89 \times 10^{-9}$  atm/m<sup>3</sup> mol (Fendinger and Glotfelty 1990), indicating a low potential for volatilization from either moist soil or water. The vapor pressure of malathion is  $3.38 \times 10^{-6}$  mm Hg (USDA/ARS Pesticide Properties Database), indicating a low potential for volatilization of the compound from dry soil surfaces. Data provided in the EPA Reregistration Eligibility Decision (RED) for malathion indicate that the compound did not appreciably volatilize ( $\leq 5.1\%$  in 16 days) from a silt loam soil when applied in three different formulations to soil samples at various moisture contents (EPA 2000a). In a study of malathion volatilization from dry quartz sand, the compound was not observed to volatilize (Mulla et al. 1981). However, several researchers have suggested the possibility of the volatilization of malathion from nonnatural surfaces, such as metals, plastic playground equipment, cement, and paved areas, based on mass deposition study data (Bradman et al. 1994; Brown et al. 1993b).

Based on the results of several studies, malathion may be removed from the atmosphere by wet deposition (Harman-Fetcho et al. 2000; McConnell et al. 1998). Dry deposition of malathion does not appear to occur; the compound is generally present in the atmosphere in a vapor phase rather than as a particulate, although it may exist adsorbed to particulate matter (Bossan et al. 1995; Mulla et al. 1981). Malathion and its oxon degradate, malaoxon (also present in the parent compound as an impurity), have both been detected in the water phase of fog (Rice 1996). Malathion has been observed in fogwater collected from pristine remote areas, indicating that it may be transported away from locations of use (Rice 1996).

The water solubility of malathion is relatively high from an environmental fate perspective, at 145 mg/L (25 °C), leading to a high potential for its transport in surface water and groundwater (Mulla et al. 1981). Additionally, malathion generally does not adsorb significantly to soils, leading to a high potential for its leaching through soils and into groundwater. However, the actual presence of malathion in water will also depend on the persistence of the compound, which is generally longer at acidic pHs. Data from several studies summarized in a review paper indicate that malathion has been detected in both surface water and groundwater, and that its presence may be attributed to either direct application or contamination from indirect sources (Mulla et al. 1981). Based on information contained in a database for pesticides in groundwater that was compiled by EPA from monitoring data available for 1971–1991, malathion was detected in a total of 12 wells in three states (California, Mississippi, and Virginia), at concentrations ranging from 0.007 to 6.17 µg/L; monitoring data were reported for a total of 3,252 wells (EPA 1992).

## 6. POTENTIAL FOR HUMAN EXPOSURE

Malathion has been observed to be very highly mobile to highly mobile in sandy loam, sand, loam, and silt loam soils, with Freundlich  $K_d$  values of 0.83–2.47 (EPA 2000a). However, the corresponding  $K_{oc}$  values (151–183) for the four soils indicate that malathion may also be classified as moderately mobile in the soils. At the concentrations (not reported) tested in the batch equilibrium study, the soil adsorption isotherms were found to be linear, indicating that adsorption was independent of concentration (EPA 2000a). It is noted, however, that malathion is rapidly degraded in the soil, with a half-life of <1 week (Mulla et al. 1981). Therefore, despite the potentially high mobility of the compound in soil, leaching of malathion through the soil into groundwater may not be a significant factor affecting the fate of the compound in the environment.

Although data on the mobility of malathion in U.S. soils were relatively scarce in the literature, adsorption of malathion has been shown to be related to the soil organic matter content as well as the cation exchange capacity of the soil clay fraction. MacNamara and Toth (1970) reported that in a laboratory study of the adsorption of malathion to three clay mineral systems (kaolinite, illite, and montmorillonite) and a humic acid system, greater adsorption was observed in the humic acid system relative to the clay mineral systems. Among the clay mineral systems, the adsorption of malathion increased with the increasing cation exchange capacity of the soils; adsorption did not appear to be correlated with pH. These researchers also demonstrated that the adsorption of malathion was greater in soils with greater amounts of soil organic matter, and that the destruction of the soil organic matter fraction of soils led to decreased adsorption; the pH of the soil:solution test systems (pH 4.5–6.7) was not observed to be correlated with adsorption (MacNamara and Toth 1970). Studies conducted on non-U.S. soils have also demonstrated that the adsorption of malathion is significantly correlated to the soil organic matter or organic carbon contents, with greater adsorption observed in soils with higher organic matter or organic carbon contents (Bell and Tsezos 1987; Khan and Khan 1986; Sujatha and Chacko 1991).

The bioconcentration factor (BCF) for malathion in aquatic organisms has been reported for several types of organisms. In a review, Howard (1991) reported malathion BCF values of 7.36 for lake trout, 29.3 for Coho salmon, a range of 150–1,917 (mean of 869) for white shrimp (*Penaeus setiferus*), and a range of 200–1,667 (mean of 959) for brown shrimp (*P. aztecus*); malathion did not bioconcentrate in a freshwater fish (Motsugo; *Pseudorasbora parva*). In a Japanese study, it was reported that malathion bioconcentrated in the freshwater fish willow shiner (*Gnathopogon caeruleus*) with a mean BCF of 34.4 (Tsuda et al. 1989).

## 6. POTENTIAL FOR HUMAN EXPOSURE

In the EPA RED for malathion, BCF values ranging from 23 to 135 were reported for whole bluegill sunfish, while a range of 4.2–18 was reported for the edible tissue of the fish (EPA 2000a). These results, reported to EPA by the malathion registrant, and those reported in Howard (1991) do not clearly indicate whether bioconcentration in aquatic organisms is an important fate process for malathion that would allow for the potential for biomagnification of malathion residues in the food chain. However, it was also reported to EPA that 96 and 73% of the malathion residues depurated from the whole and edible fish tissues, respectively, during a 14-day depuration period. Additionally, residue analysis indicated that the parent compound was partially metabolized in the fish, with 33.3–35.9% of the residues present as the degradate malathion monocarboxylic acid and 5.7% of the residues present as 1 of 22 other compounds including malathion dicarboxylic acid, malaoxon, demethyl malathion, monoethylfumarate, and oxalacetic acid (EPA 2000a). Additionally, in a review paper, Niimi (1987) reported that the half-life of malathion in the muscle tissue of carp was 1 day. These data indicate, despite the apparent tendency of malathion to partition into the tissues of aquatic organisms, that the potential for biomagnification in the food chain is likely to be low because malathion appears to be metabolized by the aquatic organisms.

No data were found in the literature on the partitioning of malathion into and within plants.

### 6.3.2 Transformation and Degradation

In general, malathion is degraded in the environment through two main pathways, activation and degradation (Mulla et al. 1981). Activation of the compound involves oxidative desulfuration, yielding the degradate malaoxon, a cholinesterase inhibitor with greater toxic properties than its parent compound. Activation may be achieved by photooxidation, chemical oxidation, or biological activation, the latter of which occurs enzymatically through the activity of mixed function oxidases (Mulla et al. 1981). Degradation of malathion occurs through both chemical and biological means, with hydrolysis being the most important pathway for each (Konrad et al. 1969). Biological degradation through the hydrolytic pathway is mainly achieved through the enzymatic activity of carboxylesterases and phosphatases, and to a lesser extent through the activity of reductase (Laveglia and Dahm 1997; Mulla et al. 1981). Malathion may also be degraded through des- or dealkylation of the *O*-methyl or *O*-ethyl groups, mediated by a phosphatase/mixed-function oxidase system (Laveglia and Dahm 1977; Mulla et al. 1981).

## 6. POTENTIAL FOR HUMAN EXPOSURE

**6.3.2.1 Air**

Pesticides may be transformed and degraded in the atmosphere due to photolysis and by reaction with ozone, hydroxyl, and nitrate radicals. Very little definitive information was found in the literature on the transformation and degradation of malathion in air. Bradman et al. (1994) stated that both malathion and malaoxon are unstable in the atmosphere and that reported half-lives for the two compounds in air range from a few hours to 1 day; however, a review of the original papers cited in Bradman et al. (1994) do not directly support this statement for malathion and malaoxon specifically (Atkinson et al. 1989; Goodman et al. 1988). In a review paper, Mulla et al. (1981) stated that although the effects of light (including ultraviolet [UV] radiation) on both malathion and its degradate malaoxon have been studied, little is understood of the transformation of the parent to malaoxon through photolysis. Howard (1991) reported an estimated atmospheric photooxidation half-life of 1.5 days based on the reaction of malathion with photochemically produced hydroxy radicals. Based on the scarce data available in the literature, it appears that malathion degradation in the atmosphere occurs mainly due to indirect photolysis (photo-oxidation) rather than resulting from direct photolysis. In a photodegradation study of malathion exposed to natural sunlight and UV irradiation (maximum wavelength of 360 nm) as thin films on glass, the compound was relatively stable to sunlight and exhibited only slight degradation (16%) by 25 hours under UV light; none of the six degradates were present at >0.01% (Chukwudebe et al. 1989). In a non-U.S. study of malathion adsorbed to fly ash (particulate matter), Bossan et al. (1995) determined that adsorbed malathion is photodegraded when exposed to irradiation of >290 nm for up to 1.5 hours, but does not degrade when adsorbed to kaolin. Malathion on fly ash decreased by up to 70% of the adsorbed compound following 40 minutes of irradiation. However, the study authors attributed the degradation of malathion on fly ash to the presence of metals and metal oxides in the fly ash.

**6.3.2.2 Water**

Malathion in water undergoes chemical and microbial degradation. The rate and extent of its degradation is dependent on the chemical and physical properties of the water system, particularly temperature and the solution pH, in addition to the composition of the microbial population present in the system.

Malathion is degraded rapidly by hydrolysis at more alkaline pH levels, but is stable to hydrolysis at acidic pHs (Wolfe et al. 1975, 1977). In a review paper, Mulla et al. (1981) noted that malathion was instantaneously degraded by hydrolysis at pH 12; had a half-life of approximately 1 day at pH 11; was

## 6. POTENTIAL FOR HUMAN EXPOSURE

rapidly degraded at pHs 9 and 7.7, with respective half-lives of approximately 12–24 hours and >3 days; did not degrade at pH  $\leq 6.2$  by 3 days; and was hydrolytically stable in acidic solution (pH >2). A half-life of 6.21 days has been reported for malathion at pH 7 (EPA 2000a). Wolfe et al. (1975) reported a half-life of >1 year at pH 4. Chapman and Cole (1982) reported half-lives of 18 weeks at pH 4.5, 5.8 weeks at pH 6.0, 1.7 weeks at pH 7.0, and 0.53 weeks at pH 8.0. In an unpublished study submitted to EPA, malathion was observed to degrade to some extent at pH 5, with approximately 20% degradation by 28 days (EPA 2000a). These data indicate that, in general, under conditions typically encountered in the environment, where pH is commonly 5–9, hydrolysis is expected to be a significant fate process at all but the more acidic pH levels (i.e., pH 5 and 6).

It has been demonstrated that temperature also has an effect on the hydrolysis of malathion. The rate of hydrolysis of malathion has been reported to increase by a factor of 4 (4X) for each 10 °C increase in temperature (Mulla et al. 1981). A half-life of 1.3 days at pH 7.4 has been reported for malathion at a temperature of 37.5 °C, with a corresponding half-life of 10.5 days reported for that pH when the temperature was decreased to 20 °C (Freed et al. 1979a). It has also been demonstrated that the temperature of the water system has an effect on the hydrolysis products at alkaline pHs (Wolfe et al. 1975, 1977). Observed hydrolysis products included malathion monoacids, *O,O*-dimethylphosphorodithioic acid, and diethyl fumarate. Wolfe et al. (1975, 1997) reported that two competing processes, carboxyl ester hydrolysis and *O,O*-dimethyl phosphorodithioic acid elimination, were occurring, with the former process being favored at lower temperatures. These researchers also reported that the  $\alpha$ -monoacid was more prevalent than the  $\beta$ -monoacid (85:15), and that malathion monoacids are approximately 18 times more stable than the parent compound under similar alkaline conditions. Under alkaline conditions, the potential degradate malathion diacid was determined to be approximately 200 times more stable than the parent compound under similar alkaline conditions (Wolfe et al. 1975).

A study on the oxidation of malathion to malaoxon in oxygen-saturated water under acidic conditions demonstrated that oxidation by molecular oxygen is not a significant fate process in the environment (Wolfe et al. 1975, 1977). Malathion was stable in oxygen-saturated water under acidic conditions for up to 2 weeks.

Malathion may also be transformed in the water by indirect photolysis, but appears to be relatively stable to direct photolysis based on the limited data available in the literature. Wolfe et al. (1975) demonstrated that malathion was photolytically stable in distilled water (pH 6) when exposed to irradiation with wavelengths of >290 nm, but degraded with an observed first half-life of 16 hours in natural water

## 6. POTENTIAL FOR HUMAN EXPOSURE

obtained from the Suwannee River which contained “a large amount of colored materials.” It is assumed that the referenced “colored materials” are derived from humic acids which, as known photosensitizers, can contribute to indirect photolysis in water systems. Aside from the early studies referenced here, very little other information on the photolysis of malathion in water was found in the literature. In a non-U.S. study, the rapid degradation of malathion in natural (estuarine) water exposed to ambient sunlight and temperature was reported; the half-life of malathion in estuarine water from the Ebre Delta area of Spain was 4.4–4.9 days (LaCorte et al. 1995). The contribution of photolysis to the overall degradation rate for the compound was not determined. In a study of malathion in river water, sea water, and groundwater in Hawaii, Miles and Takashima (1991) found that although degradation was rapid (mean half-life of 4.7 days), photodegradation and biodegradation of the compound were not important; degradation proceeded mainly by an elimination reaction. Based on these data, the direct photolysis of malathion in water is not an important fate process.

Microbial degradation of malathion in water has been studied in different types of water. A study was conducted to determine the degradation rate of malathion at 20 °C in sterile (autoclaved; pH 8.20) and unsterile (pH 8.05) filtered seawater and in a seawater/sediment (pH 7.3–7.7) microcosm (Cotham and Bidleman 1989). Reported half-lives were 3.3 days in sterile seawater, 2.4 days in unsterile seawater, and 2 days in the seawater/sediment microcosm. When the values determined for the seawater systems were normalized to pH 8.0, the half-life of malathion was approximately twice as long in sterile seawater, at 5.3 days, as in unsterile seawater (half-life of 2.6 days; Cotham and Bidleman 1989). These researchers noted that the more rapid degradation in the seawater/sediment system relative to the unsterile seawater system, which had a higher pH (leading to more rapid hydrolysis), indicates that microbial activity or interaction of malathion with the sediment was a contributing factor (in addition to hydroxide-catalyzed hydrolysis) to the degradation of the compound. Half-lives of 92–96 hours for malathion (1 mg/L) in seawater were reported by Bourquin (1977); significant malathion degradation was not observed in sterile seawater. Degradation products observed in the study were malathion monocarboxylic acid and malathion dicarboxylic acid; malaoxon was not detected as a degradation product.

In a study of the degradation of malathion by isolated salt-marsh microorganisms, 11 of the 15 bacterial cultures were able to degrade malathion as a sole carbon source and the remaining 4 were able to degrade malathion by cometabolism when 0.2% peptone was added as an additional source of carbon (Bourquin 1977). An isolated salt-marsh fungus was unable to degrade malathion without the addition of 0.2% peptone. The study author attributed the degradation of malathion by bacterial cultures to a carboxylesterase system that leads to the formation of the mono- and dicarboxylic acids, and a delayed

## 6. POTENTIAL FOR HUMAN EXPOSURE

demethylation reaction that leads to the formation of demethyl-malathion. Delayed phosphatase activities leading to phosphorylated derivatives, which act as cholinesterase inhibitors in fish, were also cited (Bourquin 1977). Complete mineralization of malathion was observed to be more rapid (initial appearance of CO<sub>2</sub> at 2 versus 7 days) with a mixed microbial culture than with the individual cultures.

A study was conducted to determine the ability of fungi to degrade malathion in aquatic environments using a species of fungus (*Aspergillus oryzae*) isolated from a freshwater pond (Lewis et al. 1975). Although the study authors stated that the rate of transformation of malathion in the lab could not be extrapolated to the field, it was determined, based on comparisons with data obtained previously, that malathion was degraded 5,000 times more rapidly by bacteria versus the fungus. The main degradate of the fungal degradation of malathion,  $\beta$ -malathion monoacid, was the same degradate produced by bacterial degradation of malathion (Lewis et al. 1975).

### 6.3.2.3 Sediment and Soil

In soils and sediments, microbial degradation (mainly through enzyme-catalyzed hydrolysis) and hydrolysis are important degradation processes for malathion. Studies have demonstrated that this is particularly true at higher pH values and soil moisture contents (Miles and Takashima 1991). Malathion degrades rapidly in soil, with reported half-lives in soil ranging from hours to approximately 1 week (Gibson and Burns 1977; Howard 1991; Konrad et al. 1969). Bradman et al. (1994) reported a range of half-life values of <1–6 days for malathion and 3–7 days for malaoxon in soil based on data obtained from the literature. Miles and Takashima (1991) reported respective half-lives of 8.2 and 2 hours for malathion in Hawaiian soil in the laboratory and the field.

In a review paper, Mulla et al. (1981) reported that biological degradation of malathion proceeds mainly through hydrolysis catalyzed by enzyme systems including carboxylesterases and phosphatases; malathion is also degraded by des- or dealkylation by means of phosphatase or mixed-function oxidase (MFO) enzyme systems. In a review paper on the degradation of organophosphorus insecticides in soil, Laveglia and Dahm (1977) stated that the predominant pathway for the biodegradation of malathion is carboxylesterase activity. Degradates observed in studies of the microbial degradation of malathion include malathion monoacid, malathion dicarboxylic acid, potassium dimethyl phosphorothioate, potassium dimethyl phosphorodithioate, and demethyl phosphorodithioate (Mulla et al. 1981). Other potential malathion degradates resulting from biodegradation by individual species of microorganisms

## 6. POTENTIAL FOR HUMAN EXPOSURE

include malaoxon, inorganic phosphate, thiophosphate, monomethyl phosphate, dimethyl phosphate, and diethyl maleate (Laveglia and Dahm 1977).

Konrad et al. (1969) observed a more rapid initial degradation of malathion in sterile soils than in an inoculated aqueous system in which malathion did not undergo biodegradation until after a 7-day lag period, indicating that actual biodegradation of the compound requires acclimation by the microbial population. In a study on the degradation of malathion in sterile and nonsterile soils, these researchers also found that the degradation rate of malathion was more rapid in soils that exhibited more rapid initial adsorption of the compound (Konrad et al. 1969). The study authors concluded that the degradation of malathion in soil is directly related to the adsorption of the compound to the soil surfaces, which serves to catalyze the degradation process and allows for almost immediate degradation of the compound. Based on the results of the study, the researchers also concluded that (direct) biodegradation by soil microorganisms does not play an important role in malathion degradation in soils (Konrad et al. 1969). Other researchers have also concluded that the degradation of malathion in soil is mainly due to exoenzymes in some soils, and is a combination of microbial metabolism; exoenzyme activity, particularly in the organic matter fraction of the soil; and hydrolysis (Gibson and Burns 1977).

In a study on the cometabolism of malathion in soil, Merkel and Perry (1977) found that the presence of certain cosubstrates (alkanes and 1-alkenes) increased the rate of malathion biodegradation in soil from a tobacco field and sediment from an estuary of the Neuse River in North Carolina. Compared with a control (unamended system), the addition of 1-heptadecene and n-heptadecane each increased the rate (2–3 times) of metabolically produced  $^{14}\text{CO}_2$  in the soil system; acetate, succinate, pyruvate, and citrate did not effectively serve as cosubstrates for the oxidation of malathion in either of the soils studied.

Data on the photodegradation of malathion on soil were scarce in the available literature. In a photodegradation study of malathion exposed to natural sunlight and UV irradiation (maximum wavelength of 360 nm) as thin films on glass, the compound was relatively stable to sunlight and exhibited only slight degradation (16%) by 25 hours under UV light; none of the degradates were present at >0.01% (Chukwudebe et al. 1989). In the EPA RED for malathion, a photodegradation on soil half-life of 173 days was reported for a pH 6.5 sandy loam soil (EPA 2000a). Based on these limited data, photodegradation on soil is not likely to be a significant fate process for malathion in the environment.

## 6. POTENTIAL FOR HUMAN EXPOSURE

**6.3.2.4 Other Media**

Limited data were found on the degradation of malathion in or on plants. In a Canadian study conducted to determine the persistence of malathion on strawberry plots, malathion decreased rapidly in strawberry flowers and immature fruits (Bélanger et al. 1990). In the first year of the study, malathion decreased to 2.7% of the initial concentration within 2 days of application and was 1.5% within 7 days; in the second study year, malathion decreased to 4.35% of the initial concentration by 3 days. Mulla et al. (1981) reported that degradation of malathion in plants, as in soil and water, occurs mainly by means of hydrolysis at the P-S bond; carboxylesterase-mediated hydrolysis is also of great importance.

**6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT****6.4.1 Air**

In a study conducted in the fall of 1991 to determine the individual concentrations of 23 commonly used indoor pesticides, including malathion, in indoor ambient air and dust, air samples were collected from two rooms each of seven homes in New Jersey at two heights, 25 and 75 cm, to represent the breathing space of a child while crawling and standing, respectively, and dust samples were collected from vacuum cleaners (Roinestad et al. 1993). Malathion was not detected (respective detection limits of 1 and 50 ng/m<sup>3</sup>) in the air or dust collected from any of the seven homes.

A study was conducted to determine the presence of 10 pesticides, including malathion, in the ambient air of the storage rooms (5 of which were located in buildings separate from the offices) and offices of 10 commercial pest control firms in North Carolina during the summer (August) and winter (February) of 1993; an inventory taken in February 1993 indicated that 5 of the 10 companies had malathion in storage at that time (Wright et al. 1996). Malathion was detected in 23 of the samples, at a mean concentration of 0.77 µg/m<sup>3</sup> and at a range of 0.02–3.57 µg/m<sup>3</sup>, with the maximum concentration found during the summer in an office of a company in which the offices and storage rooms were located in one building. The compound was detected in the air of both offices and storage rooms during both the summer and winter, including in the air of a storage room that did not have malathion listed on the inventory.

Airborne pesticide residues were determined from air samples collected along the Mississippi River from Louisiana to Minnesota during a 10-day period in June of 1994. Malathion, which is used minimally for

## 6. POTENTIAL FOR HUMAN EXPOSURE

agricultural purposes within the 40-km zone near the river, was detected at all 10 sampling times during the 10-day study; the highest levels of detection corresponded with the major metropolitan areas near or along the sampling route. The maximum concentration (0.25 ng/m<sup>3</sup> detection limit) of malathion was 4.6 ng/m<sup>3</sup> (near New Orleans, Louisiana), with a range of 0.14–4.6 ng/m<sup>3</sup>; the median concentration was 0.23 ng/m<sup>3</sup> (Majewski et al. 1998).

A review of published data was conducted to determine the presence of pesticides in atmospheric fog in both agricultural and nonagricultural areas of the United States (Rice 1996). The presence of malathion has been reported most frequently in the San Joaquin Valley of California during the dormant spraying season (January–February) when dense fog events occur frequently in the California's Central Valley. Reported concentrations of malathion plus malaoxon (in a 1:0.9 ratio) in atmospheric fog over agricultural areas have ranged from 0.07 to 8.7 µg/L, with the maximum concentration observed in Monterey, California in January 1985; concentrations of 0.14–0.30 and 0.90–3.0 µg/L have been reported for malathion and malaoxon, respectively, for nonagricultural areas of Monterey, California. Concentrations of <0.0032 µg/L have been reported for malathion in fog over the Bering/Chukchi Sea, a pristine remote ecosystem (Rice 1996).

A study was conducted to determine the wet deposition of current-use pesticides, including malathion, in the Sierra Nevada Mountain Range in the Central Valley of California in the winter and spring of 1995 and 1996; rain and snow samples were collected from two sites in Sequoia National Park (SNP) and one site in the Lake Tahoe Basin (McConnell et al. 1998). In the four counties closest to Sequoia National Park in California's Central Valley, 28,683 kg of malathion were applied to approximately 900,000 acres of harvested cropland (mainly cotton) in 1995, with the peak release period occurring in March. Malathion was detected in 53% of the collected wet deposition samples from SNP, at <0.046–24 ng/L in samples from the lower SNP elevation and <0.045–6 ng/L in samples from the higher SNP elevation; malathion was present at <0.046–18 ng/L in the Lake Tahoe Basin samples.

Following repeated aerial applications of malathion, at a target rate of 23.8 mg/m<sup>2</sup>, to urban/residential areas (1,500 km<sup>2</sup>) of southern California between August 1989 and July 1990 to eradicate medflies, the CDFA Environmental Monitoring Branch measured the mass deposition, air concentrations, and selected water concentrations of malathion and its primary oxidation product, malaoxon (Bradman et al. 1994). The mean mass deposition of the malathion originally released to the air (during the first application only) at a target rate of 23.8 mg/m<sup>2</sup> was 22.1 mg/m<sup>2</sup>, with a range of 1.7–53.7 mg/m<sup>2</sup> (Bradman et al. 1994). The mean concentration of malathion in the air was 25.1 ng/m<sup>3</sup> during the aerial spraying period,

## 6. POTENTIAL FOR HUMAN EXPOSURE

increased to a maximum of 61.6 ng/m<sup>3</sup> within 24 hours of spraying, and was 3.3 ng/m<sup>3</sup> within 96–120 hours of spraying (Brown et al. 1993b). The mean concentration of malaoxon in the air was 5.4 ng/m<sup>3</sup> during the spraying, was a maximum of 48.1 ng/m<sup>3</sup> within 24–48 hours of spraying, and was 4.5 ng/m<sup>3</sup> within 96–120 hours of spraying (Brown et al. 1993b).

#### 6.4.2 Water

Several studies have been conducted to determine the presence and concentration of malathion in runoff waters as well as in surface waters of various river basins in agricultural areas of the United States. Malathion was not detected (detection limit of 35 ng/L) in storm water runoff (from rice fields and fruit orchards) within the Sacramento River Basin, California, following a storm event in January 1994 (Domagalski 1996). In a study of pesticides in the streams of an agricultural and an urban area of Colorado, conducted from April 1993 to April 1994, 25 water samples were collected each from the Lonetree Creek Basin near Greeley, Colorado (an agricultural land-use area), and the Cherry Creek Basin (urban area) near Denver, Colorado; 2 of the samples in the agricultural area and 7 of the samples in the urban area were collected during storm runoff events (Kimbrough and Litke 1996). Malathion was not detected (detection limit of 0.014 µg/L) in the water samples from the agricultural area, but was present in approximately 30% of the samples from the urban area, at a maximum concentration of 0.16 µg/L; statistical analysis of the data indicated that concentrations of malathion were significantly higher in the storm runoff event samples than in the nonstorm samples.

In a study of pesticide fluxes in nine surface water bodies of the Mississippi River Basin, the concentrations of 26 pesticides, including malathion, were monitored between May 1991 and March 1992 at nine sites, including three sites on the Mississippi River and six sites located near the mouths of major tributaries of the Mississippi (Larson et al. 1995). Malathion was detected (detection limit of 0.005 µg/L) at only two of the eight sites for which data were reported. In the White River Basin, the malathion flux as percentage of the total agricultural usage of malathion (0.98 metric tonnes or 980 kg) in the river basin was 0.12% (1.18 kg); in the Missouri River Basin, the malathion flux was <0.01% (8.5 kg) of the total agricultural usage (85 metric tonnes or 85,000 kg) in the river basin.

A study was conducted in 1990 to determine the presence of pesticides and polycyclic aromatic hydrocarbons (PAHs) in the subsurface and microlayers of the Winyah Bay and North Inlet in South Carolina; samples were collected at seven locations every 2 months during the year-long study (Kucklick and Bidleman 1994). Malathion, used for mosquito control in the populated areas of coastal South

## 6. POTENTIAL FOR HUMAN EXPOSURE

Carolina, was detected (detection limit of 0.5 ng/L) in the subsurface water at a maximum mean concentration of 32 ng/L, with a range in individual samples of below the limit of detection to 47 ng/L. In the surface microlayer (top  $\leq 1$  mm) samples, malathion was detected at a maximum mean concentration of 32 ng/L, with a range in individual samples of below the limit of detection to 57 ng/L.

Monitoring studies have been conducted to determine the presence of numerous pesticides, including malathion, in groundwater in the United States. In a review of pesticides in groundwater monitoring data in the literature, Ritter (1990) reported that malathion occurrence in groundwater from normal agricultural use was reported in the literature for only one state. In a database of pesticides in groundwater that was compiled by EPA from data available for 1971–1991, results indicated that malathion was detected in a total of 12 wells in three states (California, Mississippi, and Virginia) at concentrations ranging from 0.007 to 6.17  $\mu\text{g/L}$ ; monitoring data were reported for a total of 3,252 wells (EPA 1992). Forty-one land-use studies were conducted in 1993–1995 at a total of 1,034 agricultural and urban sites representing 20 major hydrologic basins throughout the United States to assess the occurrence of 46 pesticides, including malathion, in shallow groundwater for the National Water-Quality Assessment (NAWQA) program; 31 of the studies were in agricultural areas and 10 were in urban areas (Kolpin et al. 1998). Malathion was detected (detection limit of 0.005  $\mu\text{g/L}$ ) at 0.2% of all sites, with detection frequencies of 0.4% for sites where corn and alfalfa growth accounted for  $>20\%$  of the crops grown there, and 1.7% for sites where orchards or vineyards accounted for  $>50\%$  of the crops (Kolpin et al. 1998).

### 6.4.3 Sediment and Soil

To estimate soil concentrations following an aerial application of malathion, at a target rate of 23.8  $\text{mg/m}^2$ , to urban/residential areas (1,500  $\text{km}^2$ ) of southern California between August 1989 and July 1990 for the eradication of medflies, mass deposition data for malathion and its primary oxidation product, malaoxon, were obtained from the CDFA Environmental Monitoring Branch (Bradman et al. 1994). Based on measured values of mass deposition, daily malathion and malaoxon residue levels in soil were estimated for a single application using two sample mixing depths. Based on a mixing depth of 1 cm, soil concentrations of the parent and its degradate were estimated as 1.4 and 0.01  $\mu\text{g/g}$ , respectively; based on a mixing depth of 0.1 cm, the corresponding estimated concentrations in soil were 14.1 and 0.10  $\mu\text{g/g}$  (Bradman et al. 1994).

In a study of 49 randomly chosen agrichemical facilities located throughout Illinois, malathion was detected in soil samples at 6 of the 18 sites that handled the compound (Krapac et al. 1995). Malathion

## 6. POTENTIAL FOR HUMAN EXPOSURE

was detected in 11 of the soil samples from the six sites (a total of 822 samples were collected from the 18 total sites in the study), at a mean concentration of 125 µg/kg (ppb) and at a concentration range of 31–690 µg/kg; the common range of detections was 22–100 µg/kg.

No monitoring data were found in the available literature for malathion detections in sediment.

### 6.4.4 Other Environmental Media

Monitoring studies have been conducted to determine the presence of malathion residues in/on food and feeds. Malathion residues were present, at 0.05–>2.0 ppm, in 249 of the 19,851 samples of food and animal feeds tested by the FDA in fiscal years 1982–1986; the selection of test samples was not random, but was geared toward choosing samples most likely to contain pesticide residues based on various factors (Luke et al. 1988). The malathion degradate malaoxon was detected in only two of the samples. In an FDA monitoring study of organohalogen and organophosphorus pesticide residues in 545 domestic surveillance samples of mixed feed rations conducted during fiscal years 1989–1994, malathion was the most commonly detected pesticide, occurring in 425 of the samples (in trace amounts in 53 of those samples) and accounting for approximately 53% of all pesticide residues detected (Lovell et al. 1996). Malathion was detected in the samples at a concentration range of 0.006–4 ppm, with a median concentration of 0.098 ppm. In a study conducted in 1977 to determine malathion residues on and in oranges following low-volume (100 gal/ac) and dilute applications (1,500 gal/ac) to orange trees in California, malathion residues on and in unwashed whole fruits were below the then current residue tolerance levels of 8 ppm (Carman et al. 1981). In the edible portion (pulp) of the fruits, malathion residues were 0.01–0.03 ppm 7 days after treatment and <0.01 ppm 30 days after treatment; the authors stated that the results indicated that the majority of the residues were present in or on the orange rinds.

## 6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

There are insufficient data to determine the potential daily inhalation and dermal exposure levels for the general population, although estimates of daily exposure to malathion in air at two U.S. sites have been reported (Whitmore et al. 1994). Based on the results of that study and on the information presented in Sections 6.3 and 6.4, exposure levels for the general population are likely to be low by these routes. Inhalation exposure is not considered to be important for the general population, with the possible exception of those individuals living in or near areas where malathion is frequently sprayed or those

## 6. POTENTIAL FOR HUMAN EXPOSURE

individuals using a low pressure handwand for mosquito and household pesticide control (EPA 2000a). Since malathion is adsorbed through the skin, dermal contact is a more relevant pathway, compared with inhalation, for the general population, and may be of even greater importance for those who apply malathion for home and garden use. Dermal exposure to malathion for the general population may also be more important for persons living near sites where malathion is sprayed for public health usage or where off-target drift from Boll Weevil Eradication Programs occurs (EPA 2000a). However, dermal contact is most likely to occur in people who are occupationally exposed to malathion.

As part of the National Health and Nutrition Examination Survey (NHNES II) conducted in 1976–1980, urine specimens from 6,990 people living in the United States were analyzed for selected pesticide residues to determine the occurrence of pesticide body burden residues in the general population and to estimate the extent of human exposure to pesticides in the general U.S. population. Residues of malathion monitored in the study included malathion dicarboxylic acid (DCA) and malathion alpha-monocarboxylic acid (MCA). The degradates MCA and DCA were detected in samples from 1.1% and 0.5% of the 6,990 study participants, respectively, at a maximum concentrations of 970 ng/mL (ppb) and 250 ng/mL, respectively (Kutz et al. 1992). Based on the results of the study, it was estimated that 1,800,000 and 800,000 persons in the general U.S. population would have quantifiable MCA and DCA in their urine samples, indicating recent exposure to malathion (Kutz et al. 1992).

In a study of selected pesticide metabolites in urine, conducted in Maryland for a single year during 1995–1996, MacIntosh et al. (1999a) found the malathion metabolite DCA in 6.6% of 347 samples, at a maximum concentration of 51.0 µg/L (and 51.0 µg/g creatinine).

In a study conducted to determine human exposure to selected pesticides in drinking water, conducted in Maryland during 1995–1996, MacIntosh et al. (1999b) did not find malathion above the limit of detection (0.043 µg/L) in any of the drinking water samples.

In the EPA's Non-Occupational Pesticide Exposure Study conducted at two U.S. sites (Jacksonville, Florida and Springfield/Chicopee, Massachusetts) during 1986–1988, it was determined that 17–32% of the Jacksonville population was exposed to detectable levels of malathion in the indoor air during the three sampling seasons (summer, spring, winter) utilized at that site; 0–4% of the population was exposed to malathion in the outdoor air and 11–15% of the population was exposed to malathion in their personal space air (Whitmore et al. 1994). The maximum concentrations of malathion in the indoor air in Jacksonville for the three seasons ranged from 14.9 to 20.8 ng/m<sup>3</sup>; maximum concentration ranges for the

## 6. POTENTIAL FOR HUMAN EXPOSURE

outdoor air and the personal space air were 0–0.3 and 9.2–16.8 ng/m<sup>3</sup>, respectively. At the Massachusetts site, 0–2% of the population was found to be exposed to malathion in the indoor air during the two sampling seasons (spring and winter) utilized at that site; 0–5% of the population was exposed to malathion in the outdoor air and 0–4% of the population was exposed to malathion in their personal space air (Whitmore et al. 1994). Measurements conducted in spring showed a mean concentration of malathion in the indoor air at the Massachusetts site of 5.0 ng/m<sup>3</sup>, a mean of 0.8 ng/m<sup>3</sup> was detected outdoors, and 0.5 ng/m<sup>3</sup> was found in personal air space; no malathion was detected in winter. Mean daily air exposure estimates were determined for each of the two sites so that the values could be compared with dietary exposure estimates; the respective mean air exposure estimates for the Florida and Massachusetts sites were 232 and 8 ng/day (Whitmore et al. 1994). Based on dietary exposure estimates made using data from FDA Total Diet Studies and dietary recall questionnaires, it was determined that dietary exposure to malathion residues was much greater than exposure to residues in air for the populations of both the Florida and Massachusetts sites. Dietary exposure to malathion residues for the periods 1982–1984, 1986–1987, and 1987 ranged from 4,510 to 4,701 ng/day for the Florida site population, and was 4,625 ng/day for the Massachusetts site population in 1982–1984 (Whitmore et al. 1994). These results indicate that the inhalation route of malathion exposure is much less important than the ingestion route for the general populations of the two sites studied.

In an assessment of exposure to malathion and malaoxon in areas of southern California that had received aerial applications of malathion for public health purposes, adult, infant, and child exposures through dermal and inhalation routes were estimated and compared with a select dietary exposures (including backyard vegetables and soil); estimates of the various exposures were made for both average and high-end exposure scenarios. In general, estimated exposures to malathion residues increased with the extent of outdoor activity and with higher levels of consumption of backyard vegetables (Marty et al. 1994). The most important routes of exposure for adults were dermal exposure and ingestion exposure from consumption of contaminated, unwashed backyard vegetables, with respective estimated doses of 1–246 and 30–80 µg/kg/day; the estimated inhalation dose for adults was only 0.01–0.1 µg/kg/day (Marty et al. 1994).

The FDA Total Diet Studies (formerly referred to as Market Basket Studies) examine food for levels of pesticides. Estimates are then made of the mean intake of a pesticide per unit body weight (in µg/kg/day) using the amounts of pesticides found in foods and food consumption patterns; target groups include 6–11 months, 2 years, 14–16 years female, 14–16 years male, 25–30 years female, 25–30 years male, 60–65 years female, and 60–65 years male. Malathion was the second most frequently detected pesticide in

## 6. POTENTIAL FOR HUMAN EXPOSURE

the study conducted during June 1984–April 1986 (Gunderson et al. 1995a), occurring in 22% of the samples, and was the most frequently detected pesticide in the study conducted during July 1986–April 1991, occurring in 20% of the samples (Gunderson et al. 1995b). For the period June 1984–April 1986, the mean daily intake estimates for malathion were 0.1333  $\mu\text{g}/\text{kg}/\text{day}$  for the 6–11 months group, 0.2548  $\mu\text{g}/\text{kg}/\text{day}$  for the 2 years group, 0.0835  $\mu\text{g}/\text{kg}/\text{day}$  for the 14–16 years female group, 0.1159  $\mu\text{g}/\text{kg}/\text{day}$  for the 14–16 years male group, 0.0699  $\mu\text{g}/\text{kg}/\text{day}$  for the 25–30 years female group, 0.0796  $\mu\text{g}/\text{kg}/\text{day}$  for the 25–30 years male group, 0.0615  $\mu\text{g}/\text{kg}/\text{day}$  for the 60–65 years female group, and 0.0719  $\mu\text{g}/\text{kg}/\text{day}$  for the 60–65 years male group (Gunderson et al. 1995a). For the period July 1986–April 1991, the mean daily intake estimates for malathion were 0.1139  $\mu\text{g}/\text{kg}/\text{day}$  for the 6–11 months group, 0.2184  $\mu\text{g}/\text{kg}/\text{day}$  for the 2 years group, 0.0686  $\mu\text{g}/\text{kg}/\text{day}$  for the 14–16 years female group, and 0.0965  $\mu\text{g}/\text{kg}/\text{day}$  for the 14–16 years male group, 0.0598  $\mu\text{g}/\text{kg}/\text{day}$  for the 25–30 years female group, 0.0704  $\mu\text{g}/\text{kg}/\text{day}$  for the 25–30 years male group, 0.0567  $\mu\text{g}/\text{kg}/\text{day}$  for the 60–65 years female group, and 0.0645  $\mu\text{g}/\text{kg}/\text{day}$  for the 60–65 years male group (Gunderson et al. 1995b). FDA Total Diet Studies conducted in 1979–1980 and 1980–1982 estimated the average daily exposure to malathion was 14.0  $\mu\text{g}/\text{day}$  (Gartrell et al. 1985) and 16.8  $\mu\text{g}/\text{day}$ , respectively (Gartrell et al. 1985).

Based on an EPA risk assessment of malathion conducted, in part, using the Dietary Exposure Evaluation Model (DEEM), acute dietary exposure to malathion (plus malaoxon) from food is not a concern for the majority (95<sup>th</sup> exposure percentile) of the U.S. population (EPA 2000a). Based on a calculated acute population adjusted dose (aPAD), at which no adverse health effects would be expected using the safety factor prescribed in the Food Quality Protection Act (FQPA), the population subgroup with the highest acute dietary exposure (at 38% of the aPAD) is children aged 1–6 (EPA 2000a). For chronic dietary exposure, the population subgroup with the highest exposure (at 1.6% of the cPAD) is also children aged 1–6. However, values of <100% of the aPAD or cPAD are not considered to be of concern (EPA 2000a). The reported aPAD and cPAD values were 0.5 mg/kg/day (500  $\mu\text{g}/\text{kg}/\text{day}$ ) and 0.024 mg/kg/day (24  $\mu\text{g}/\text{kg}/\text{day}$ ), respectively. Based on these values and the results of the FDA's Total Diet Studies, dietary exposure to malathion from food is also not important for the general population. EPA also determined that dietary risk of malathion exposure from drinking water was not important for the general population (EPA 2000a).

Exposure of the general population to higher concentrations of malathion may result from contact with or ingestion of contaminated hazardous waste site media, principally soils and water. No information was found in the available literature regarding the size of the human population potentially exposed to malathion through contact with contaminated waste site media.

## 6. POTENTIAL FOR HUMAN EXPOSURE

NIOSH estimated that approximately 19,170 U.S. workers, employed in 18 occupations excluding farm work, are potentially exposed to malathion in occupational settings; of these, an estimated 1,909 are females (NIOSH 1981). Occupational exposure to malathion is mainly through the dermal route, but may also occur through inhalation. The OSHA workplace air environmental limit for malathion is 15 mg/m<sup>3</sup> (NIOSH 2001).

Agricultural workers and commercial applicators may also be exposed to malathion through occupational practices. Farm worker protection measures include routine cholinesterase monitoring of blood samples; similar monitoring is required in many states for commercial applicators who apply organophosphate insecticides (Fenske and Leffingwell 1989). For many crops, the restricted entry intervals for workers to enter fields treated with malathion following application are generally short (<1 day) relative to reentry intervals for other organophosphate pesticides (Swift 1976), although restricted entry intervals for certain activities such as hand pruning or harvesting of crops are often longer (0–6 days; EPA 2000a).

In a Department of Commerce monograph on human exposure to malathion in the workplace, Santodonato et al. (1985) reported that the number of U.S. workers exposed during (initial) production of malathion is limited since production of the chemical was limited at that time to a single corporation (American Cyanamid), but increases greatly at the formulation stage since numerous companies utilize malathion in formulated products; the production of these products requires activities such as loading, blending/mixing, and packaging. While production of malathion is no longer limited to a single corporation, it is still not widely spread.

Exposure levels for workers are affected by the type of work activity being conducted at the time of the exposure (Santodonato et al. 1985; Swift 1976). In a study of the exposure of formulating plant workers to ethion and malathion, the exposure to malathion of workers employed in various activities was determined; worker categories included mixers, baggers, and stackers (Wolfe et al. 1978). For all categories combined, the potential exposure to malathion was determined to be 150 mg/hour for the dermal route and 1.29 mg/hour via inhalation. For the dermal route, however, exposure was approximately 5–6 times greater for baggers (244 mg/hour) compared with either mixers or stackers (40–50 mg/hour). For the inhalation route, potential exposure to malathion was also much greater for baggers (2.19 mg/hour) than for mixers (0.05 mg/hour) or stackers (0.50 mg/hour). None of the exposure levels identified in the study were considered to represent a very great hazard to the formulating plant workers (Wolfe et al. 1978).

## 6. POTENTIAL FOR HUMAN EXPOSURE

Several researchers have found that worker exposure to malathion for a variety of activities (e.g., application operations, harvesting, field observation, formulating operations) using various formulation types (e.g., spray, dust, aerosol) is greater via the dermal route than through inhalation (Culver et al. 1956; Culver et al. 1956; Durham and Wolfe 1962; Jegier 1964; Lin and Hee 1998; Wolfe et al. 1978, 1967). Based on data reported in the literature, Santodonato et al. (1985) reported mean dermal exposures during malathion spraying of 2–67 mg/hour, and mean airborne concentrations of 0.6–6 mg/m<sup>3</sup>, indicating a lower potential for exposure via inhalation relative to the dermal route. In a review of worker exposure data, Durham and Wolfe (1962) reported that exposure rates for workers applying malathion as an aerosol (liquid sprays) were 6.6 mg/70-kg man/hour via the dermal route and 0.3 mg/70-kg man/hour via inhalation.

In a study of the persistence of pesticides on the hands of occupationally exposed workers, malathion was found to persist on the hands of three of eight farmers occupationally exposed to malathion; it was also found to persist for at least 7 days on the hands of a home gardener who grew fruits and vegetables treated with the compound, which was applied by the gardener without the use of protective gloves (Kazen et al. 1974). In the study, malathion was not detected on the hands of three nonoccupationally exposed workers.

In a study of occupational exposure to flea control products, including malathion, among pet handlers in California, Ames et al. (1989) found that not only the workers who applied the products, but also others (nonapplicators) who worked at the facilities where the products were used, were exposed to the chemicals. Of the 200 workers considered to be nonoccupationally exposed based on their duties, 31 of the workers reported that they were exposed to malathion in the workplace.

In a study of malathion permeation through the gloves of workers exposed to the compound, Lin and Hee (1998) reported that the highest potential for exposure was associated with worker dermal contact with pure and technical-grade malathion and the emulsifiable concentrate formulations; these formulations generally contain 30–91% (w:w) malathion. Dermal exposure to malathion varied with the type of protective gloves worn by the workers in the study, with greater protection provided by Viton and Silver Shield gloves, and the least protection provided by nitrile gloves; for the first two types of gloves, exposure following permeation through the gloves was <0.02 mg, while permeation through the latter type of glove ranged from <0.02 to 283 mg (Lin and Hee 1998). Differences in permeation mass and time of breakthrough for the nitrile gloves was related to the carrier (e.g., *m*-xylene, distilled water) in the

## 6. POTENTIAL FOR HUMAN EXPOSURE

formulated malathion product. These data indicate that in addition to the formulation type of the malathion product utilized and the activity performed by the worker, the type of protective materials or equipment used will affect the potential worker exposure levels.

**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 within the general population living in areas far from where malathion is sprayed are not likely to be exposed to high levels of malathion. An exception to this may be at homes where malathion is used extensively for home and garden use, particularly if inappropriately high application rates (relative to label recommendations) are utilized and if backyard vegetables are not washed prior to consumption. Children playing on turf following the application of malathion by means of a handgun sprayer may be exposed to malathion via the dermal route at levels high enough to cause concern (EPA 2000a).

For those children living in areas where malathion is sprayed for public health use or at homes where malathion is used extensively, children within the general population are likely to be exposed to malathion in the same ways that adults are, including through contact with sprayed plants, soil, or other surfaces; breathing contaminated air; eating contaminated foods; or drinking contaminated water. Additionally, small children are more likely than adults to be in close contact with yard dirt or playground dirt, lawns, and indoor (carpet) dust. Malathion residues bound to soil or dust particles in carpets or on bare floors may present an exposure route for infants and toddlers through dermal contact and oral ingestion. Children are known to participate in frequent hand-to-mouth activity and to have a tendency to put foreign objects into their mouths. As a result of this behavior, children may ingest malathion present

## 6. POTENTIAL FOR HUMAN EXPOSURE

in soil and dust or through direct transfer of the chemical from their skin to their mouths. Children are also lower to the ground than adults and something that may exist at arm or hand level for an adult may be at mouth level for a child.

Approximately 16–20% of the annual malathion use in the United States is attributed to general agricultural use, while 59–61% is attributed to use by the USDA in eradication programs (EPA 2000a). Approximately 0.5 million pounds of malathion are released to soil annually just through applications to agricultural sites (e.g., roads, ditches, and near buildings); this value excludes other agricultural uses (i.e., crops; EPA 2000a). Children living in agricultural areas may be exposed to higher pesticide levels than other children because of pesticides that may get tracked into the homes by household members, contact with pesticide spray drift, or from playing in the fields near where malathion has been sprayed. Dermal exposure is expected to be the most likely route of exposure once the pesticide has been applied, although oral ingestion through the direct transfer caused by hand-to-mouth activity or consumption of unwashed produce treated with malathion is also likely. Malathion is moderately to highly mobile in soil, however, indicating that it does not readily adsorb to soil particles. Additionally, it breaks down rapidly in soils, as does the primary oxidation product, malaoxon. Thus, the level of exposure that children will have to malathion is dependent on the time that has passed since the application of the compound. Also, exposure to certain levels of malathion or its residues does not mean that the compounds will be bioavailable at those levels. No U.S. data were found on exposure or body burden measurements made on children.

Approximately 3.4 million pounds of malathion are released to soil annually through applications to nonagricultural sites; this includes malathion use for medfly and mosquito control, golf courses, and home and garden use (EPA 2000a). Malathion has been sprayed over large areas for public health usage, to eradicate medflies and to control mosquito populations; approximately 8–15% of the malathion used annually in the United States is attributed to public health use (EPA 2000a). This practice may lead to exposure of malathion to children through dermal contact and ingestion when they play on treated soil surfaces or in contaminated sand boxes and perform the frequent hand-to-mouth activity common in children. To estimate exposure concentrations following repeated aerial applications of malathion to urban/residential areas (1,500 km<sup>2</sup>) of southern California for the eradication of medflies, mass deposition data for malathion and its primary oxidation product, malaoxon, were obtained from the CDFEA Environmental Monitoring Branch (Bradman et al. 1994). Based on measured values of mass deposition, malathion and malaoxon exposure concentrations (acute and chronic) were estimated for typical and high or upper bound exposure levels. Estimated malathion acute and chronic exposure concentrations for a typical exposure for the top 0.1-cm depth of soil were 14.7 and 4.9 mg/g, respectively; the corresponding

## 6. POTENTIAL FOR HUMAN EXPOSURE

values for malaoxon were 0.10 and 0.03 mg/g (Bradman et al. 1994). For outdoor surfaces, potentially including playground equipment, estimated malathion acute and chronic exposure concentrations for a typical exposure were 22.0 and 7.3 mg/g, respectively; the corresponding values for malaoxon were 0.15 and 0.05 mg/g (Bradman et al. 1994).

Malathion is widely used for residential (i.e., home and garden) purposes; approximately 10% of the malathion used annually in the United States is attributed to home and garden use (EPA 2000a). Children may be exposed to malathion used in the home or garden, or to malathion tracked into the home from outside by themselves or other household members. A Minnesota study monitored the urinary metabolite level of commonly used pesticides including malathion in 102 children, ages 3–13 years. The intrachild urinary metabolite levels were found to be greater than the detection limit 46% of the time for malathion (Adgate et al. 2001). In a nine-home pilot study to assess monitoring methods for use in determining pesticide exposure to children aged 6 months to 5 years old, malathion was not detected in any of the nine homes; however, the study authors indicated that the lack of detections may have been due to analytical limitations for the 7 of 30 targeted pesticides, including malathion, which were not detected in any of the homes (Lewis et al. 1994).

Children may be exposed to malathion brought into the home by parents or other household members who are occupationally exposed. Malathion residues may be present on the skin, hair, clothing items and shoes of workers employed in industries, such as agriculture, where malathion is used or at sites where malathion is manufactured or formulated. Exposure to children may occur through dermal contact with contaminated items. Because children are likely to be in close contact with carpet or floors, transfer of contaminated dirt from work shoes to carpeting provides a means of exposure. Respiratory exposure from contact with occupationally exposed workers is not likely to be significant.

In a study of pesticide exposure to children in the home in rural areas, samples of house dust were analyzed from a day care center and 10 homes, 5 of which were also the home of at least one farm worker (currently working in the field) and 8 of which reported home pesticide use (Bradman et al. 1997). While malathion was detected in one nonfarmworker home, at a concentration of 1.60 µg/g and a loading of 2.40 µg/m<sup>2</sup>, it was not detected in any of the homes with a farmworker as a resident. Malathion was also not detected in the day care center.

Children may be exposed to malathion and its residues in the foods that they eat. In an early (1963–1967) study of pesticide residues in prepared baby foods in the United States, the average malathion

## 6. POTENTIAL FOR HUMAN EXPOSURE

concentration was below the limit of detection (0.005 ppm); however, the pesticide was only monitored in a limited number of samples (Lispcomb 1968). In an FDA Total Diet Study conducted in 1980–1982 to determine the dietary intake of selected pesticides for infants and toddlers, the estimated average daily intakes of malathion residues were determined based on pesticide residue concentrations found in 11 food groups (Gartrell et al. 1986). The estimated average daily intake of malathion from infant diets was 1.45 µg/day; malathion was found in the grain and cereal products and the oil and fats food groups at concentrations of 0.008–0.158 ppm. The estimated average daily intake of malathion from toddler diets was 2.64 µg/day; malathion was found in the grain and cereal products, fruit and fruit juices, oil and fats, sweets and adjuncts, and beverages food groups at concentrations of less than the limit of quantification (LOQ)–0.24 ppm. Data on the weight-adjusted intake of malathion by infants and toddlers were determined based on the results of the FDA Total Diet Studies for fiscal years 1978–1981/1982 (Gartrell et al. 1986). The reported weight-adjusted intakes of malathion ranged from 0.126 to 0.331 µg/kg body weight/day for infants and were 0.193–0.299 µg/kg body weight/day for toddlers for the four study years.

Quantitative estimates of the exposure of infants and children to pesticides have been reported in the results of FDA Total Diet Studies conducted in the 1980s using the amounts of pesticide residues in foods thought to be in the diets of infants or children. Estimates of the mean intake of malathion per unit body weight were made for the 6–11 months age group, 2 year age group, and the 14–16 years female and 14–16 years male age group. For the period June 1984–April 1986, the estimates were 0.1333 µg/kg/day for the 6–11 months group, 0.2548 µg/kg/day for the 2 year group, 0.0835 µg/kg/day for the 14–16 years female group, and 0.1159 µg/kg/day for the 14–16 years male group (Gunderson et al. 1995a). The daily intake values for the 6–11 months group and the 2 year group were similar to the values determined in the FDA Total Diet Study for the same period of time in 1982–1984 (Gunderson et al. 1995a). For the period July 1986–April 1991, the mean daily intake estimates were 0.1139 µg/kg/day for the 6–11 months group, 0.2184 µg/kg/day for the 2 year group, 0.0686 µg/kg/day for the 14–16 years female group, and 0.0965 for the µg/kg/day 14–16 years male group (Gunderson et al. 1995b). Malathion residues were not detected in any of the samples of infant formula (milk-based without iron, canned, ready-to-serve) analyzed in the study (Gunderson et al. 1995b).

The FDA Total Diet Study results for fiscal years 1985–1991 include estimates of pesticide residue intakes associated with 33 types of representative infant foods, infant formula, and adult foods eaten by infants and children (e.g., raw and processed fruits, fruit juices, milk, peanut butter) that have been prepared for consumption (Yess et al. 1993). Malathion residues were found in infant foods at maximum levels of 0.001–0.008 ppm in cereals, combination meat or poultry dinners, fruits/fruit juices, and

## 6. POTENTIAL FOR HUMAN EXPOSURE

vegetables; malathion residues were not detected in samples of infant formulas. Malathion was detected in adult foods eaten by infants and children at maximum concentrations of 0.004 ppm in grape juice, 0.0005–0.0009 ppm in milk (including processed/canned and fluid), and 0.40 ppm in peanut butter.

The FDA Regulatory Monitoring Program analyzes surveillance samples of whole, unwashed, unpeeled foods that may be eaten by infants/children to determine pesticide concentrations in 10,000 domestic and imported food samples (Yess et al. 1993). During the fiscal years 1985–1991, malathion was detected in domestic samples at a maximum concentration of 0.12 ppm in apples (in 7 of 2,464 samples) and 0.036 ppm (in 9 of 862 samples) in oranges. In imported samples, malathion was detected at maximums of 0.60 ppm in bananas (in 10 of 1,097 samples), 0.02 ppm in orange juice (in 1 of 64 samples), and 0.25 ppm in oranges (in 32 of 474 samples). Based on an EPA risk assessment of malathion conducted, in part, using the Dietary Exposure Evaluation Model (DEEM), acute dietary exposure to malathion (plus malaoxon) from food is not a concern for children aged 1–6 (EPA 2000a). Based on a calculated acute population adjusted dose (aPAD), at which no adverse health effects would be expected using the safety factor prescribed in the Food Quality Protection Act (FQPA), the population subgroup with the highest acute dietary exposure (at 38% of the aPAD) and the highest chronic dietary exposure (at 1.6% of the cPAD) is children aged 1–6 (EPA 2000a). However, values of <100% of the aPAD or cPAD are not considered to be of concern (EPA 2000a). The reported aPAD and cPAD values were 0.5 mg/kg/day (500 µg/kg/day) and 0.024 mg/kg/day (24 µg/kg/day), respectively. Based on these values and the results of the FDA's Total Diet Studies, dietary exposure to malathion from food is not considered to be important for children aged 1–6.

A potential source of exposure in infants is the presence of malathion in breast milk. Malathion was detected in breast milk (5 ppb) from 1 of 11 Italian women from the general population on the 5<sup>th</sup> day postpartum, but was not detected by the 11<sup>th</sup> day (Roggi et al. 1991).

### 6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

The populations most at risk for exposure to relatively high levels of malathion are field workers who go into sprayed areas, particularly before the prescribed restricted entry intervals have passed. Also at greater risk for potentially high exposures are occupationally exposed workers who do not use adequate protective equipment that is appropriate for the type of malathion product being utilized. People who live in or near areas where malathion is sprayed for public health uses and those who consume unwashed

## 6. POTENTIAL FOR HUMAN EXPOSURE

backyard vegetables treated with malathion may also be exposed to higher levels of the chemical relative to the general population.

In an assessment of exposure to malathion and malaoxon in areas of southern California that had received aerial applications of malathion for public health purposes estimates of the various exposures were made for both average and high-end exposure scenarios. In general, estimated exposures to malathion residues increased with the extent of outdoor activity and with higher levels of consumption of backyard vegetables (Marty et al. 1994). The most important routes of exposure for adults were dermal exposure and ingestion exposure from consumption of contaminated, unwashed backyard vegetables, with respective estimated doses of 1–246 and 30–80  $\mu\text{g}/\text{kg}/\text{day}$  (Marty et al. 1994).

It has been reported that malathion was oxidized to malaoxon following its release in 1990 in the Los Angeles Basin of California for control of the Mediterranean fruit fly; concentrations of malaoxon in air were greater than those of parent malathion (Wolfe and Sieber 1993). Because malathion is less toxic in the parent (thiono) form than in its oxon form, exposure to malathion residues are potentially more harmful in situations that favor the formation of the degradate malaoxon. Such a case may occur when a dust formulation is utilized on plant or tree leaves, which allows for the formation of a catalytic surface where oxidation to malaoxon may take place, particularly in the presence of a high level of atmospheric oxidant such as ozone and in times of low humidity; these conditions are thought to be favorable to the buildup of the oxon (Wolfe and Sieber 1993). These data indicate that the restricted entry intervals that do not account for such cases may lead to higher potential exposures to workers who enter a field with such conditions too early after spraying.

## 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 malathion is 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 malathion.

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

## 6. POTENTIAL FOR HUMAN EXPOSURE

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.** The physical and chemical properties of malathion are sufficiently well characterized to allow assessment of the environmental fate of the compound to be made (Budavari 1996; Buyuksonmez 1999; Chiou et al. 1977; Fazzalari 1978; Freed et al. 1979a; Hansch et al. 1995; Howard and Neal 1992; Kim et al. 1984; Matsumura 1985; Ruth 1986; Tomlin 1997; Watanabe 1993).

**Production, Import/Export, Use, Release, and Disposal.** Malathion is commercially produced in the United States and abroad. Malathion has been commercially produced in the United States since 1950. No production volume data were located for the 1950s and 1960s; production was estimated to be 24 million pounds in 1972 (Santondonato et al. 1985; von Rumker et al. 1974) and 30 million pounds in 1983 (IARC 1983). Recent production volume data for the United States were not located. Data on import volumes are limited; import volumes for 1977 were 6,457 pounds (USITC 1978) and 143,260 pounds in 1982 (SRI 2000). U.S. exports of malathion were estimated to be 11,020,000 pounds in 1978 (SRI 2000). More current information on the production volume, import, and export of malathion is needed to make an accurate assessment of the potential for human exposure to the pesticide.

Releases to air, land, and water occur primarily through the use of malathion as an insecticide. The media of most importance for human exposure are air and soil. 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. The Toxic Release Inventory (TRI), which contains this information for 2000, became available in June of 2000. This database is updated yearly and provides a list of industrial production facilities and emissions.

The recommended methods of disposal of malathion are incineration in a furnace equipped with an afterburner and a scrubber (Sittig 1985). If incineration is not an option, malathion may be disposed of by absorbing in vermiculite, dry sand, earth, or similar material and then burying in a designated landfill (Mackison 1981). Only small amounts of malathion may be land filled (United Nations IRPTC 1985). Waste water treatment technologies have been investigated for malathion using biological treatment and

## 6. POTENTIAL FOR HUMAN EXPOSURE

reverse osmosis (EPA 1982). Another method of disposal that has been suggested for malathion is combustion in molten potassium chloride. The destruction of malathion is 99% and the products of combustion can be used as a fertilizer (United Nations IRPTC 1985).

**Environmental Fate.** There is a lack of data on the degradation (fate and persistence) of malathion in soil under both aerobic and anaerobic acidic conditions, as well as on the degradation of malathion on dry surface soils where hydrolysis is less likely to occur. Further studies with malathion are needed to assess these particular situations. Monitoring data for pesticide disposal and other hazardous waste sites are also lacking and would be useful in determining the prevalence of malathion residues at these sites. As very little definitive information was found in the literature on the transformation and degradation of malathion in air, additional studies are needed on this topic, including on the transformation of the parent to malaaxon through photolysis and on the subsequent degradation of malaaxon. Several researchers have suggested the possibility of the volatilization of malathion from nonnatural surfaces, such as metals, plastic playground equipment, cement, and paved areas, based on mass deposition study data (Bradman et al. 1994; Brown et al. 1993b). More information is needed on the potential volatilization of malathion from nonnatural surfaces such as pavements and playground equipment. Additionally, information is needed on the potential for photodegradation of malathion and malaaxon on such surfaces in order to characterize the fate of malathion in the environment when it is used over widespread areas for public health purposes. Information on the physical properties and the fate and persistence of the malathion degradate malaaxon (which is also present in malathion as an impurity) would be particularly useful in assessing the human health risks from malathion use, as the oxon is considered to be more toxic than the parent compound (EPA 2000a).

**Bioavailability from Environmental Media.** Malathion can be absorbed following inhalation or dermal contact with contaminated media, and by ingestion of contaminated water or food, particularly of unwashed backyard vegetables (Bradman et al. 1994; Brown et al. 1993b; Durham and Wolfe 1962; EPA 2000a; Kutz et al. 1992; MacIntosh et al. 1999a; Whitmore et al. 1994). Dermal contact with malathion present in soil or on treated crops and ingestion of malathion present on backyard vegetables or soil particles are exposure routes that may be of concern. No information was found in the available literature on the bioavailability of malathion following ingestion of soil or dermal contact with contaminated media; such data are needed to determine potential exposures to humans.

**Food Chain Bioaccumulation.** The majority of the data available on the bioaccumulation of malathion suggest that, while malathion may be bioconcentrated, it is rapidly metabolized or depurated

## 6. POTENTIAL FOR HUMAN EXPOSURE

from the tissue of aquatic organisms and is, therefore, not likely to be biomagnified in the food chain such that it would pose human exposure threats (EPA 2000a; Howard 1991). However, bioconcentration factor data available in the literature did not definitively show that such a concern would be unfounded. Additional data to verify (or refute) the assumption that food chain bioaccumulation of malathion is not an important fate process would be helpful in assessing human exposure risks from ingestion of contaminated fish or other aquatic organisms. Data on the uptake and potential concentration of malathion residues by plants were not found in the literature. Because malathion is utilized for home garden purposes, there is a potential for malathion to be taken up by vegetable and other produce plants. Although malathion is water soluble, malathion residues incorporated into the plants may be difficult to remove through washing or other food preparation processes and the consumption of such may provide a route for exposure. Additional data are needed on the ability of food plants to uptake malathion residues from the soil or through aboveground plant parts that come into contact with the insecticide through direct application.

**Exposure Levels in Environmental Media.** Malathion has been detected in the ambient air (Bradman 1994; Brown et al. 1993b; Majewski et al. 1998; Wright et al. 1996), precipitation (McConnell et al. 1998), fog (Rice 1996), surface water (Kimbrough and Litke 1996; Kucklick and Bidleman 1994; Larson et al. 1995), groundwater (EPA 1992; Ritter 1990), soil (Krapac et al. 1995), and in/on food and feeds (Carman et al. 1981; Lovell et al. 1996; Luke et al. 1988). Estimates of human intake of malathion have been made for ingestion of foodstuffs (EPA 2000a; Gartrell et al. 1985, 1986; Gunderson et al. 1995a, 1995b). Limited estimates of dermal and inhalation exposure have been made for the general population (Marty et al. 1994; Whitmore et al. 1994). Improved estimates of exposure from air, water, and soil as well as from treated nonnatural surfaces (such as pavements, sidewalks, and playground equipment) are needed to assess human exposure to malathion, particularly for exposures resulting from home and garden use and public health uses. Estimates of exposure to malaoxon, the production of which is favored in the environment under some conditions, are particularly important for assessing the human health risks related to malathion use. Information concerning concentrations of malathion in the air, water, and soil at the NPL hazardous waste sites known to be contaminated with malathion are needed to assess the exposure of populations living in the vicinity of these sites.

**Exposure Levels in Humans.** The malathion residues malathion dicarboxylic acid (DCA) and malathion alpha-monocarboxylic acid (MCA) may be detected in human urine samples following recent exposure to malathion (Fenske and Leffingwell 1989; Kutz et al. 1992; MacIntosh et al. 1999a). These compounds are specific for malathion when there is a history of exposure. Limited studies have been

## 6. POTENTIAL FOR HUMAN EXPOSURE

conducted to determine the occurrence of pesticide body burden residues in the general population and to estimate the extent of human exposure to pesticides in the general U.S. population (Kutz et al. 1992); to determine the exposure of human populations at two U.S. sites to malathion via dermal and inhalation routes and compare these with estimated dietary exposure in the same populations (Whitmore et al. 1994); to determine malathion exposure to adults, infants, and children in areas receiving aerial applications of malathion for public health purposes (Marty et al. 1994); and to determine exposure levels in occupationally exposed persons (Ames et al. 1989; Lin and Hee 1998; Wolfe et al. 1978). However, a population that is potentially exposed to malathion through home and garden use of the compound also exists. Within occupationally exposed populations, subgroups of persons who may be exposed to higher levels of malathion exist; these include workers who don't wear adequate protective materials/equipment and workers who may enter too early into treated areas that have conditions favorable to the buildup of malaoxon. Information on the body burdens and intake of malathion residues for these populations and subgroups would be useful in assessing the exposure levels of persons with potentially high exposures to malathion. This information is necessary for assessing the need to conduct health studies on these populations.

**Exposures of Children.** The exposure of children to malathion through ingestion of foodstuffs eaten by infants and children has been estimated fairly extensively for various age groups including infants, toddlers, and teenagers (EPA 2000a; Gunderson et al. 1995a, 1995b), and weight-adjusted intakes have been calculated (Gartrell et al. 1986). However, only limited studies have been conducted to estimate the extent of the exposure of children to malathion residues through dermal and inhalation pathways or through the ingestion of contaminated soil (Bradman et al. 1994). Data on the body burden measurements of malathion made on children are needed to determine exposures to children, particularly to those children living in or near areas where malathion is sprayed for public health purposes or used in the home and garden. Also, additional studies on the exposure of children to malathion on natural outdoor surfaces such as fields and turf, and on nonnatural outdoor surfaces such as sidewalks and playground equipment in areas where malathion is widely sprayed are necessary to determine the health risks to children living in such areas. Studies are also needed to determine breast milk contamination by malathion in order to assess exposures to nursing infants.

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

## 6. POTENTIAL FOR HUMAN EXPOSURE

**Exposure Registries.** No exposure registries for malathion were located. This chemical is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to malathion.

### 6.8.2 Ongoing Studies

Information on ongoing studies related to the physical and chemical properties; the production, use, release, and disposal; the environmental fate and exposure; and the bioavailability of malathion was scarce. The Federal Research in Progress (FEDRIP 2002) database provides additional information obtainable from a few ongoing studies that may fill in some of the data needs identified in Section 6.8.1. With the exception of one study being funded by the U.S. Geological Survey (USGS), all of the studies identified in the FEDRIP database are being funded by the USDA. The majority of the studies identified in the database abstracts that mentioned malathion tend to be for research that deals with identifying alternative compounds, including chemically based alternatives and biopesticides, that are of lower risk or safer to use compared with malathion. Other studies focus on finding improved methods of application, which would lead to the safer, more accurate, and more timely application of pesticides, including malathion. Related studies focused on studying aspects of the boll weevil, a target pest for which malathion is used in USDA eradication programs, in order to find more environmentally sound and more cost effective ways (including decreased usage of pesticides) of achieving the goal of boll weevil eradication. The use of ultra-low volume (ULV) applications for control of boll weevils or mosquitoes are mentioned in several of the research abstracts, as is the implementation of integrated pest management (IPM) programs. Some of the studies focus on the use of safer and more efficacious biological and chemical compounds to be used for the control of riceland mosquito populations that have exhibited a high tolerance to malathion.

A literature search in an additional database identified a few studies related to the use, disposal, exposure, and environmental fate of malathion.

Researchers at Mississippi State are conducting a study funded by Agricultural Research Service (ARS)/USDA to identify methods to improve the efficiency of the production of channel catfish in aquaculture. Because malathion use (as ULV applications) for boll weevil eradication in the local study

## 6. POTENTIAL FOR HUMAN EXPOSURE

area is potentially problematic for the catfish industry, the study includes experiments intended to determine the bioaccumulation of malathion in catfish tissue. Additional experiments in the study focus on the malathion degradation in aquarium and pond water.

Scientists at the University of Hawaii are conducting research funded by Cooperative State Research, Education, and Extension Service (CSREES)/USDA to help in obtaining minor use and specialty use pesticide clearances and to assist in the maintenance of current pesticide registrations. Proposed uses for individual pesticides are evaluated and prioritized based on several factors including safety to man, non-target organisms and the environment. Uses being studied for malathion include application of the insecticide on multiple fruit, nut, and vegetable crops as well as ornamentals.

Scientists at Cornell University are conducting research funded by CSREES/USDA to elucidate mechanisms of degradation and identify degradation products of various pesticides using various analytical methods. The main objective of the study is to develop a new kinetic model that will allow the researchers to evaluate the Anodic Fenton Treatment system, a newly developed technology for degrading/mineralizing pesticides and pesticide wastes (such as rinsate). The study will include the assessment of the toxicity, at both the molecular and cellular level, of the post-treatment aqueous effluent.

Researchers at the University of Maryland are measuring the concentrations of pesticides including malathion and combustion-derived polycyclic aromatic hydrocarbons in the air and water of the Chesapeake Bay. The object of the study is to understand the transport processes as well as the chemical-biological mechanisms that influence pesticide volatilization and transport. This includes studying the impacts of deposited volatiles and development of means to reduce volatile emissions. The study will also include an evaluation of the spatial and temporal trends in atmospheric transport and deposition of pesticides and combustion-derived chemicals to the Chesapeake Bay.

Scientists at the Connecticut Agricultural Experiment Station will examine pesticide exposure through non-dietary routes at commercial agricultural operations, public facilities, and in the home environment. The potential routes of non-dietary exposure to be examined include: dermal exposure by touching and handling contaminated items; non-dietary ingestion arising from hand to mouth contact with contaminated surfaces; continuous dermal exposure as a result of wearing contaminated clothing; and respiratory exposure from the inhalation of airborne contaminants.

