6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

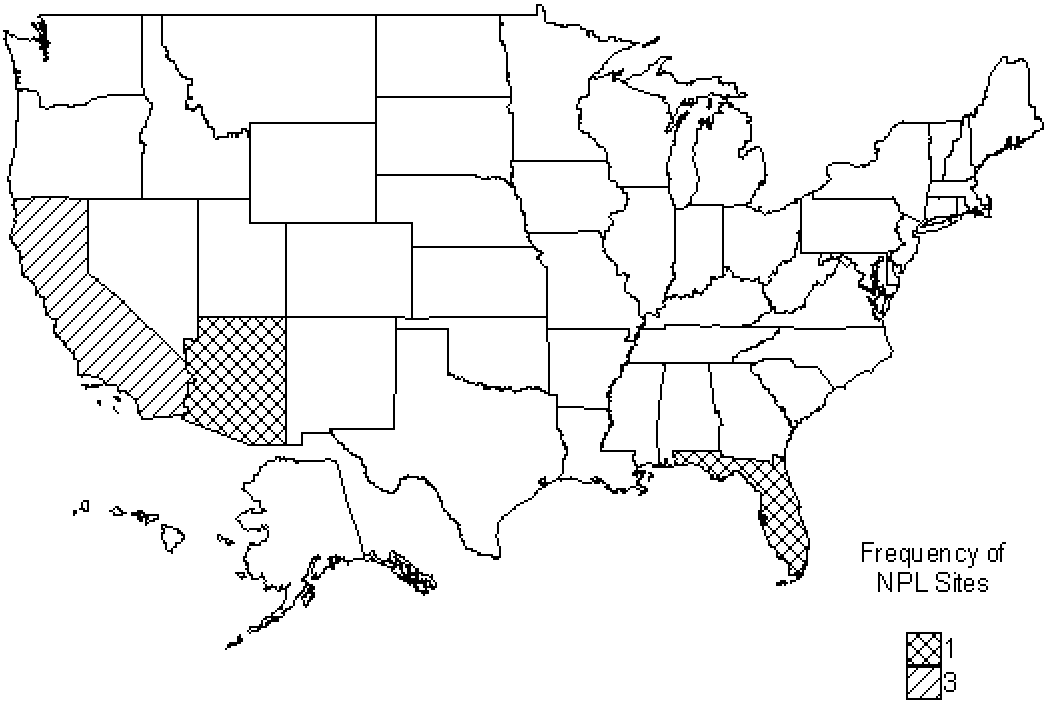
Guthion has been identified in at least 5 of the 1,699 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 2008). However, the number of sites evaluated for guthion is not known. The frequency of these sites can be seen in Figure 6-1.

Guthion is a restricted use organophosphate insecticide that is primarily used as a foliar application against phytophagous insect pests on fruit, field, or vegetable crops and works as both a contact insecticide and a stomach poison. In 2001, the EPA proposed the immediate cancellation of most uses of guthion. The only crops that guthion can still be applied to are almonds; apples/crabapples; blueberries, lowbush and highbush; Brussels sprouts; cherries, sweet and tart; nursery stock; parsley; pears; pistachios; and walnuts. On August 8, 2007, the companies that produce guthion voluntarily requested to amend their registrations which would effectively terminate certain uses (Brussels sprouts and nursery stock) of guthion by September 30, 2007 (EPA 2007). Uses on walnuts, almonds, and pistachios are scheduled to cease by October 30, 2009, and all other uses would be terminated by September 30, 2012 (EPA 2007). The application rate of guthion varies depending upon which crop it is applied to, but is typically in the range of 0.3–1.4 pounds a.i./A (EPA 1999a).

Guthion is not considered highly persistent in the environment, and degrades by a combination of biotic and abiotic mechanisms. Biodegradation occurs readily in soils and water under aerobic conditions with half-lives on the order of several days to a few weeks. Hydrolysis and photolysis are also important degradation pathways for guthion in water, foliage, and soils. In the atmosphere, vapor-phase guthion is quickly degraded by photochemically produced hydroxyl radicals; the half-life for this reaction in air is on the order of a few hours. Particulate-phase guthion is removed from the atmosphere by wet and dry deposition processes. Guthion has moderate to low mobility in soils. Its leaching potential is considered low, and therefore, guthion is only occasionally detected in groundwater.

Levels of guthion in the environment can vary considerably. In areas where it is not used, it is rarely detected, suggesting that long-range transport of this chemical does not occur. However, guthion is frequently detected in surface water bodies near fields or orchards where it has been applied as an insecticide. The most important route of exposure to guthion for the general population is through the ingestion of foods, especially vegetables and fruits that have been sprayed with this insecticide. Ingestion of contaminated drinking water, inhalation exposure, and dermal exposure to guthion are expected to be

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



Derived from HazDat 2008

low for the general population. Agricultural workers, their families, and persons residing near crops that are treated with guthion are expected to have much greater frequency of exposure and the potential to be exposed to higher levels of guthion than the general population.

6.2 RELEASES TO THE ENVIRONMENT

The amount of guthion used in the United States, and thus released to the environment, appears to be declining. The total amount of guthion used in 1997 was reported as 2,091,014 pounds, which was an 18% decrease from the amount used (2,548,867 pounds) in 1992 (USDA 2000). In 2002, the estimated annual agricultural use of guthion had declined to about 1.2 million pounds, nearly a 50% decline from 1997 (USGS 2007). Recent restrictions on the crops that guthion can be applied to are likely to result in lower emissions in future years.

There is no information on releases of guthion to the environment from manufacturing and processing facilities because these releases are not required to be reported (EPA 1998c).

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2005). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ 10 or more full-time employees; if their facility is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005).

6.2.1 Air

There is no information on releases of guthion to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 1998c).

Guthion releases to the atmosphere arise from its use as an insecticide where it is applied to crops by aerial application or with ground-based boom sprayers. Guthion was detected in air samples at one of the five current or former NPL hazardous waste sites where it was detected in some environmental media (HazDat 2008).

6.2.2 Water

There is no information on releases of guthion to the water from manufacturing and processing facilities because these releases are not required to be reported (EPA 1998c).

Guthion is released to water from point source discharges, spray drift from aerial applications, and runoff and erosion of treated soils. A multi-year study from 1981 to 1984 was conducted to determine the loadings of carbofuran, fenvalerate, and guthion to Lake Oconee in Georgia from the treatment of a pine seed orchard adjacent to the lake (Bush et al. 1986). A series of approximately 85 rainfall events over a 49 month period produced varying amounts of runoff and erosion loadings into the lake. For example, guthion was applied aerially in April of 1981 and a rainfall event 10 days postapplication produced 1,540 μg/L of guthion in the resultant runoff water (Bush et al. 1986). The amount of spray drift entering the lake was estimated by placing a series of 9 glass fiber disks within the treatment zone of the orchard and 12 discs along the edge of the lake. The discs within the treatment zone averaged 1,201 μg of guthion per disc, while the discs adjacent to the lake averaged 1.2 μg of guthion per disc (Bush et al. 1986).

Two field runoff studies were submitted by the Bayer Corporation to the EPA in support of the registration of guthion (EPA 1999a). These two studies were conducted on cotton fields in Colquitt County, Georgia and Benoit, Mississippi. A single application of guthion at an application rate of 0.25 pounds a.i./A was made in August 1989 to the Mississippi field. Eight applications of guthion (0.25 pounds a.i./A) were made at 3-day intervals starting on August 1 at the Georgia location. At the Mississippi site, a total of 14.9 g of guthion was released in runoff from the 5.2-acre plot during a heavy rainfall event that produced 3.08 inches of precipitation 2 days postapplication. Approximately 31.5% of the precipitation was accounted for in runoff from the plot during the rainfall event (EPA 1999a). A total of 13.3 g of guthion was released in runoff from the 9-acre portion of the Georgia field in four storms which occurred on August 8 (32 mm of precipitation), August 26 (61 mm of precipitation), August 31 (37 mm of precipitation), and October 1 (33 mm of precipitation). These produced 3.6, 8.3, 1.3, and 0.0012 g of guthion in the collected runoff, respectively (EPA 1999a).

Guthion was detected in the groundwater at one of the five current or former NPL hazardous waste sites where it was detected in some environmental media (HazDat 2008). There were no detections of guthion in surface water at any of these sites.

6.2.3 Soil

There is no information on releases of guthion to the soil from manufacturing and processing facilities because these releases are not required to be reported (EPA 1998c).

Guthion is released directly to soils from its registered use as an insecticide (EPA 1999a). Deposition to the ground following aerial spraying or direct applications via chemigation or sprinkler irrigation systems is common. Guthion was detected in soil samples at three of the five current or former NPL hazardous waste sites where it was detected in some environmental media (HazDat 2008). There were no detections of guthion in sediment at any of these sites.

6.3 ENVIRONMENTAL FATE

6.3.1 Transport and Partitioning

The vapor pressure of guthion is 2.2×10^{-7} mm Hg (Suntio et al. 1988) and its estimated Henry's law constant is 3.7×10^{-9} atm-m^3/mol, calculated from its vapor pressure and water solubility (EPA 1999a). These values suggest that guthion is essentially nonvolatile from water and soil surfaces. The volatilization flux of guthion from treated walnut orchards was estimated using the EPA's SCREEN-2 dispersion model (Woodrow et al. 1997). The estimated volatilization flux from the surface of the walnut tree leaves was 0.067 μg/m^2-second, which resulted in an estimated atmospheric concentration of approximately 0.23 μg/m^3 15 m downwind from the application site.

In the atmosphere, postapplication spray drift is an important source of environmental contamination and is responsible for much of guthion's transport outside of its target zone. The amount of spray drift is influenced by meteorological conditions such as wind speed and method of application (e.g., aerial or ground spraying). Droplet size, humidity, and temperature are also important factors that can affect spray drift. In general, fine droplet size, low humidity, and warm temperatures enhance the likelihood of increased spray drift. For most spray applications of pesticides, buffer zones are required between the target crop and any permanent water bodies. These buffer zones for guthion typically range from 25 feet for ground applications using boom sprayers to 150 feet for aerial applications to certain crops. Guthion may be removed from the atmosphere by wet and dry deposition. This is confirmed by the detection of guthion in atmospheric rainwater samples (Section 6.4.1). The short atmospheric residence time of guthion suggests that it will not be transported long distances from its initial release point.

Adsorption/desorption experiments using three different soils suggest that guthion has moderate to low mobility in soil and the potential to leach into groundwater is considered low. The K_{oc} values of guthion in a sandy loam (1.6% organic carbon), silt loam (2.9% organic carbon), and clay loam (0.3% organic carbon) were calculated as 475, 579, and 3,266, respectively from the Freundlich adsorption coefficients (EPA 1999a). The adsorption characteristics of guthion in five standard European soils have also been studied (Gawlik et al. 1998). The K_{oc} values in these five reference soils ranged from 534 to 4,644. The physical properties of these soils and corresponding adsorption coefficients are shown in Table 6-1.

The mobility of guthion in soils under field conditions has been studied in two alfalfa fields located in California (EPA 1999a). In the first field, a single application of guthion was made to a portion of the field at 3 pounds a.i./A. In another section of the field, two applications of 3 pounds a.i./A were made 7 days apart. The soil type of the field was described as Salinas silt that was slightly alkaline (pH 6.9–8.0). Over the course of 60 days, guthion was only detected in one soil sample below a depth of 6 inches, suggesting very limited mobility in the field. The same experimental protocol was employed in the second field located in Fresno, California. Guthion was not detected in any soil samples below a sampling depth of 6 inches in this field (EPA 1999a). Guthion was not detected below a depth of 30 cm when applied at an application rate of 9 pounds/A to a potato field with a soil texture that was described as a sandy loam and irrigated with 27.6 cm of water (Yaron et al. 1974). An aged soil column leaching study indicated that guthion and its degradation products are not particularly mobile in soils and the potential to leach into groundwater is low (EPA 1999a). Following application of an unspecified amount of ^{14}C labeled guthion to a soil that was aged for 28 days and then dried before being packed into the column, 90% of the radioactivity was located in the top 5 cm of the column after application of 35.5 cm of water over 45 days. A total of 4.4% of the radioactivity leached from the bottom of the 30.5 cm column.

The uptake and translocation of guthion in bean plants and barley has been demonstrated (Al-Adil et al. 1973). The authors reported that guthion was readily absorbed through the roots and transported undegraded to other parts of the plant following incorporation into the soil or during direct application to the leaves. The assimilation of guthion by the roots and the translocation of the radiocarbon into the aerial parts of both plant species were most rapid during the first 24 hours. On day 8, the majority of the

Table 6-1. Soil Adsorption Characteristics of Guthion in Five European Soils

Property	Vertic Cambisol (Italy)	Rendzina silt loam (Greece)	Dystric Cambisol loam (Wales)	Orthic Luvizol silt (France)	Orthic Podzol loamy sand (Germany)
pH	5.1	7.4	5.2	6.5	3.2
Percent clay	75%	22.6%	17%	20.3%	6%
Percent organic carbon	1.3%	3.7%	3.45%	1.55%	9.25%
K_d	60.37	19.0	18.4	8.6	75.4
1/n[a]	0.82	0.90	0.91	0.88	0.81
K_{oc}	4,644	487	534	556	815

[a] The parameter 1/n relates to the linearity of the adsorption isotherm. Generally, values close to 1 indicate a highly linear adsorption isotherm.

Source: Gawlik et al. 1998

residues (98%) identified were of the undegraded parent compound. Topical application to the stem and seed injection with guthion also indicated translocation of the residues throughout the plant system.

Based on its low mobility in soil, guthion is expected to adsorb to suspended solids and sediment in the water column. Guthion applied at a nominal application rate of 20 μg/L to the surface of a 2 ha pond was not detected in sediment samples 3 hours postapplication; however, guthion levels in sediment gradually increased to a maximum concentration of 62.7 μg/kg 4 days postapplication (Knuth et al. 2000). The levels gradually decreased to 11.9 μg/kg 8 days postapplication and then continued to decrease at a near constant rate to 2.05 μg/kg 50 days postapplication. Sediment samples collected at days 92, 120, and 366 had no measurable levels of guthion (detection limits 0.20 μg/kg). Accounting for the total mass balance in the pond, the authors concluded that both the aqueous phase and the sediment compartment are important environmental sinks for guthion applied to the water surface.

There are little data regarding guthion's potential to bioconcentrate in aquatic organisms, and conflicting conclusions have been reported. According to an environmental fate and exposure assessment for guthion conducted by the EPA, bioconcentration and bioaccumulation are not expected based upon the log K_{ow} value of guthion. An estimated bioconcentration factor (BCF) of 26 was calculated from a log K_{ow} of 2.75 (Hansch et al. 1995) and a regression-derived equation (Meylan et al. 1999). This BCF value suggests that the potential for guthion to bioconcentrate and biocaccumulate in aquatic organisms is low. However, experimental studies using constructed ecosystems indicate that guthion may bioconcentrate in aquatic organisms. Guthion formulated as an emulsifiable concentrate and applied to the surface of a 2-ha pond near Duluth, Minnesota at a nominal application rate of 20 μg/L showed accumulation in fathead minnows (Knuth et al. 2000). The level of dissolved guthion in the water column and the amount of guthion in adult fathead minnows were used to calculate lipid corrected BCF values. A maximum lipid corrected BCF value of 3,003 was observed 3 hours postapplication, while a minimum value of 1,027 was observed 1 day postapplication. Eight days postapplication, the BCF gradually increased to 2,254 (Knuth et al. 2000). Although these data indicate a high degree of bioconcentration, the whole-body BCF values in the minnows are substantially lower. Using the author-reported mean lipid content of 2.12% in the fathead minnows, the maximum whole-body BCF value is approximately 64 (3 hours postapplication), and the minimum value is approximately 22. These whole-body BCF values indicate that bioconcentration in aquatic organisms is low to moderate. These data are consistent with the findings of uptake and accumulation studies conducted using catfish. Catfish exposed to guthion had a relatively low magnitude of accumulation with rapid uptake and excretion (California EPA 2004). The accumulation factor was approximately 60 during the last 21 days of the 28-day exposure period. Guthion and the desmethyl oxygen analog were observed in fish tissue. Approximately 67 and 85% of the residues were excreted within 5 hours and 4 days, respectively, after exposure was discontinued.

6.3.2 Transformation and Degradation

In general, guthion is not considered highly persistent in the environment. The dominant degradation mechanism in air is reaction with photochemically produced hydroxyl radicals and direct photolysis. In water, a combination of biodegradation, hydrolysis, and photolysis is expected to result in the degradation of guthion. Biodegradation appears to be the dominant degradation process for guthion in soils, and foliar degradation by photolysis is likely to limit the persistence of guthion on treated crops.

6.3.2.1 Air

Guthion has a vapor pressure of 2.2×10^{-7} mm Hg at 20 °C (Suntio et al. 1988), which suggests that it will exist in both the vapor and particulate phases in the ambient atmosphere. Vapor-phase guthion is expected to be rapidly degraded through reaction with photochemically produced hydroxyl radicals and direct photolysis. An estimated hydroxyl radical rate constant of 1.5×10^{-10} cm^3/molec-second was estimated for guthion using a structure-estimation method (Meylan and Howard 1993). This corresponds to an atmospheric half-life of approximately 2.5 hours, assuming an atmospheric hydroxyl radical concentration of 5×10^5 molec/cm^3 (Atkinson 1985). In a direct photolysis study, thin films of guthion exposed to summer sunlight at Riverside, California degraded with an approximate half-life of 8.2 hours calculated using data by Chukwudebe et al. (1989). Three photodegradation products were observed including thiophosphoric acid O,S,O'-trimethyl ester, dithiophosphoric acid O,S,S'-trimethyl ester, and dithiophosphoric acid O,S,O'-trimethyl ester.

6.3.2.2 Water

Guthion is degraded through a combination of biotic and abiotic mechanisms in water, and is not considered persistent under environmental conditions. The hydrolysis half-lives of guthion at 30 °C in aqueous buffered solutions at pH 4, 7, and 9 were 49, 26, and 3.7 days, respectively (EPA 1999a). At 40 °C the half-lives were 23, 13, and 1.8 days at pH 4, 7, and 9, respectively. A wide variety of metabolites were formed during these experiments and in general, initial concentration and temperature did not appear to affect the amount of each degradation product that was produced. Mercaptomethyl benzazimide was formed at 4.9–10.4% after 30 days at pH 7. Hydroxymethyl benzazimide and benzazimide, which were measured as a single analyte, were found after 30 days at 8.1–12.2% at pH 4, 6.0–14.2% at pH 7, and 32.4–38.9% at pH 9. Anthranilic acid was also identified as a degradation product of guthion. Anthranilic acid was formed at 18.1–22.8% of the parent at 30 days in the pH 9 test systems. An unidentified metabolite was observed in the pH 9 test systems at 7.4–14.5% of the initially applied amount. Bismethyl benzazamide sulfide was also found at concentration <10% of the applied radioactivity.

The aqueous photolysis half-life of guthion maintained at pH 4.35 and 30 °C and exposed to natural sunlight conditions in Kansas City, Missouri was calculated as 76.7 hours (EPA 1999a). Two major degradation products were identified, benzazimide and anthranilic acid. It was noted that each metabolite is actually a complex of two degradates that could not be separately identified by the analytical procedure used in the study. The benzazimide complex consisted of benzazimide and (1N)-methoxybenzazimide, while the anthranilic acid complex consisted of anthranilic acid and methyl anthranilate ester. Benzazimide complex represented 39.1% of the radiolabeled residues at the end of the experiment, while the anthranilic acid complex reached 7.2% of the radiolabeled residues at the end of experiment.

An aerobic aquatic metabolism study was described that resulted in the formation of several degradation products of guthion; however, no rate data were supplied with this study (EPA 1999a). The degradation products identified were: des-methyl guthion, des-methyl guthion S-methyl isomer, methyl benzazimide, methylsulfinyl methyl benzazimide, methylsulfonyl methyl benzazimide, methyl benzazimide sulfonic acid, methylthiomethyl benzazimide, and either/or hydroxy-methyl benzazimide/benzazimide. The last two degradates were unresolved by the chromatographic method used for analysis. The only metabolite observed at >10% of the nominal concentration was methyl benzazimide sulfonic acid (EPA 1999a).

The degradation kinetics of guthion in a mixture of 19 organophosphate and organonitrate pesticide solutions at the ppb level was measured in ultra-pure distilled water, natural seawater, river water, and filtered river water (Lartiges and Garrigues 1995). The experiments were conducted at two temperatures (6 and 22 °C), three pH levels (pH 6.1, 7.3, and 8.1), and in both the absence of light and under natural sunlight illumination in Bordeaux, France during the months of February to July. The experimental details and results are summarized in Table 6-2. In general, increasing pH led to greater degradation due to the base-catalyzed hydrolysis reaction of guthion; however, both hydrolysis and biodegradation appear to be attenuated at low temperatures. Degradation of guthion was enhanced considerably when the solutions were exposed to natural sunlight. Similar experimental results were obtained by Medina et al. (1999), using filtered and unfiltered water from the Limon River in Venezuela. The half-life of guthion was 23.5 days in filtered river water that was maintained under dark conditions and 13.4 days in filtered

Table 6-2. Aqueous Degradation Rate of Guthion

	pH	Half-life (days)		
		6 °C	22 °C	Outdoor sunlight[a]
MQW	6.1	415	115	No data
River water	7.3	278	42	8
Filtered river water	7.3	506	35	No data
Seawater (salinity 25 g/L)	8.1	No degradation	26	11

[a] The temperatures under natural environmental conditions ranged from -2 to 25 °C.

MQW = ultrapure water from a Millipore apparatus

Source: Lartiges and Garrigues 1995

river water that was illuminated with natural sunlight. The half-life decreased to 6.1 days for nonfiltered river water exposed to sunlight during the course the experiments (Medina et al. 1999).

The effect of chlorinating drinking water and the consequence that this has on organophosphate pesticides has been addressed (EPA 2002). Chemical oxidation of the thiophosphate group leads to the formation of guthion oxygenated metabolites (oxons), which were shown to be more stable than the parent compound in chlorinated systems. In water samples amended with sodium hypochlorite to yield a total chlorine residue level of 2 mg/L, guthion at a nominal concentration of 0.5 μg/L was transformed to its oxon, with a half-life of approximately 2 hours. After 24 additional hours, only 10% degradation of the oxon was observed.

6.3.2.3 Sediment and Soil

Guthion undergoes biodegradation, photolysis, and hydrolysis in soils at varying rates depending upon the physical characteristics of the soil such as moisture, pH, and percentage of organic matter. Environmental conditions such as ambient temperature and amount of sunlight also affect the persistence of guthion. Since sunlight is rapidly attenuated as a function of soil depth and hydrolysis is only significant in moist alkaline soils, biodegradation is likely to be the major transformation pathway for guthion under ordinary environmental conditions. A soil photolysis half-life of 180 days was reported for guthion applied to a sandy loam soil (pH 5.1) during the month of January in Kansas City, Missouri (EPA 1999a). In a subsequent study, the estimated half-life was 66 days when guthion was applied to sterile sandy loam soil (pH 7) and exposed to natural sunlight (California EPA 2004). After correcting for nonphotolytic degradation, the estimated half-life was 241 days. No degradation products were identified in either of these two experiments.

The aerobic degradation of ^{14}C labeled guthion in a sandy loam soil was studied under laboratory conditions over the course of a 1-year incubation period (EPA 1999a). The time for 50% dissipation (DT_{50}) was 27 days and the DT_{90} of guthion in this soil was 146 days. Although it was observed that the degradation rate did not closely follow first-order kinetics, a nonlinear regression of the concentration versus time profile yielded an estimated half-life of 32 days (EPA 1999a). No single identified metabolite was found at >10% of the initially applied radioactivity; the oxygen analog of guthion peaked at 5.3% of the applied radioactivity 186 days after application. Four metabolites, mercaptomethyl benzazimide, hydroxymethyl benzazimide, benzazimide, and bismethyl benzazamide sulfide, were reported as a single metabolite, with a maximum of 12% of the applied amount observed at 120 days postapplication. Only

4.1% of residues were trapped as $^{14}CO_2$. The majority of the radioactivity (72%) was in unidentified soil-bound residues at the end of the experiment. Under anaerobic conditions, the estimated half-life of guthion in soil was calculated as 66 days (EPA 1999a).

Field dissipation studies using alfalfa fields in California indicated a fairly rapid rate of dissipation. Guthion applied at a rate of 3 pounds a.i./A in August to a Salinas silt loam (pH 6.9–8.0) located in Watsonville, California had a DT_{50} of 9 days (EPA 1999a). A similar experiment was conducted using an alfalfa field in Fresno, California during the month of May. The soil type in this field was characterized as a Hesperia fine sandy loam (pH 7.6–8.7). The DT_{50} was 2 days in this soil following a single application at 3 pounds a.i./A (EPA 1999a). Both of these fields are somewhat more alkaline than typical soils, which may account for the relatively rapid rate of degradation.

The DT_{50} of guthion in laboratory studies employing four different soils from Italy ranged from 4 to 20 days (Diaz Diaz et al. 1995). The shortest dissipation times were observed in alkaline soils that were high in organic matter. The soil properties and the experimental results of this study are summarized in Table 6-3.

When the initial guthion concentration in soil is very high (for example, in the case of an accidental spill), its persistence is expected to be much longer than when applied under general agricultural use conditions. Guthion, applied as an emulsifiable concentrate to plots of soil at initial levels of approximately 25,000–70,000 mg/kg (ppm), had DT_{50} values of up to 1 year, and measurable levels remained in the treated soil for up to 8 years (Staiff et al. 1975).

6.3.2.4 Other Media

Foliar wash off and foliar degradation are important environmental fate processes for guthion applied to plant surfaces. The presence of sensitizing agents in leaves and vegetation can result in enhanced photolysis, thus increasing the degradation rates of pesticides in sunlight (Floesser-Mueller and Schwack 2001). Foliar degradation half-lives on plants and leaves have been reported to range from 1.6 to 16.0 days for guthion (EPA 1999a). Louisiana sugarcane crops treated with guthion at an application rate of 0.82 kg/ha (3 times annually) had foliar dissipation half-lives of approximately 2–8 days (Granovsky et al. 1996).

Table 6-3. Soil Properties and Degradation Rate of Guthion in Four Italian Soils

Soil type	pH	Percent organic matter	Percent clay	Percent silt	Percent sand	DT_{50} (days)[a]
Sandy	7.70	0.7	12.8	8.7	76.8	20
Orchard	7.41	8.8	17.3	22.7	61.2	4
Agricultural	7.38	3.7	18.8	23.4	60.8	5
Volcanic	4.86	4.1	21.2	28.3	52.2	12

[a] DT_{50} is the time required for 50% dissipation of the initially applied amount of guthion.

Source: Diaz Diaz et al. 1995

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to guthion depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of guthion in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on guthion levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable and the presence/detection of guthion does not necessarily indicate an adverse biological effect. The analytical methods available for monitoring guthion in a variety of environmental media are detailed in Chapter 7.

6.4.1 Air

Guthion has been infrequently detected in atmospheric samples collected throughout the United States. Weekly composite rainfall samples that were obtained in urban and agricultural regions of the Midwestern United States and along the Mississippi River indicated a low frequency of detection for guthion from April to September 1995 (Majewski et al. 2000). Guthion was not detected in any samples of rainfall from a background location (Eagle Harbor, Michigan) where it had no known use. Guthion was detected in approximately 10% of the rainfall samples collected in agricultural areas of Mississippi and in approximately 5% of the rainfall samples collected in an urban area (Jackson, Mississippi). Guthion was not detected in rainfall samples obtained in either agricultural or urban areas of Iowa, but was detected in approximately 1% of the rainfall samples collected in an agricultural location in Minnesota (Majewski et al. 2000). During the same collection period, guthion was identified, not quantified, in approximately 20% of the vapor-phase and particulate-phase air samples collected from Rolling Forks, Mississippi (agricultural location), but was not detected in air samples collected in Jackson, Mississippi (Coupe et al. 2000; Foreman et al. 2000).

Guthion was detected in 36% of the atmospheric samples obtained near locations in Kern and Glenn Counties, California where it was being used as an insecticide on almond crops (Baker et al. 1996). The 24-hour mean concentration was 0.035 $\mu g/m^3$ and the maximum concentration was 0.11 $\mu g/m^3$. The maximum concentration observed in the air at the application site was 1.6 $\mu g/m^3$ (Baker et al. 1996). During application of insecticides to an apple orchard in Massachusetts approximately 1 acre in size by airblast ground sprayers, guthion applied at 0.75 kg/ha was detected downwind of the spray zone (75 feet away) at a maximum concentration of 3.87 $\mu g/m^3$ (Clark et al. 1991). Within 2 hours, the atmospheric level was reduced to 0.031 $\mu g/m^3$ as deposition processes transported the insecticide to the ground.

6.4.2 Water

Guthion has moderate to low mobility in soils and therefore has limited potential to leach into groundwater. Biotic and abiotic degradation that occurs in soils may also limit the leaching potential of guthion. Guthion was only detected (detection limit 0.001 μg/L) in 4 out of 2,451 groundwater samples collected from 1992 to 1996 in 20 major hydrological basins across the United States (Kolpin et al. 2000). The maximum observed concentration in these four positive samples was 0.18 μg/L. Guthion was not detected in 94 shallow groundwater wells sampled in 1992 in the Midwestern United States (Kolpin et al. 1995). In a compilation of groundwater data from 1971 to 1991, the EPA initially reported that guthion was detected in 5 out of 30 wells sampled in the state of Virginia in 1987 at levels ranging from 0.04 to 2.87 μg/L (EPA 1992b). According to an environmental fate and exposure assessment for guthion, these values are incorrect (EPA 1999a). According to this risk assessment there were 16 detections of guthion obtained from 60 wells sampled in July and August of 1987 in Clarke and Frederick County in the Shenandoah Valley. However, guthion was not detected in 1,598 other wells sampled in California, Indiana, Georgia, Hawaii, Maine, New York, Oklahoma, Rhode Island, or Texas from 1983 to 1991 (EPA 1992b, 1999a). Guthion was not detected in 68 wells sampled in 12 counties of California from July 1, 1994 to June 30, 1995 (California EPA 1995).

Very little data exist for guthion in finished drinking water; however, limited monitoring data suggest that its occurrence is not widespread. In a cumulative risk assessment for organophosphate pesticides, the EPA Office of Pesticide Programs (OPP) performed a 2-year pilot reservoir monitoring study of raw and finished water data for 18 active organophosphate parent compounds and 13 transformation products (EPA 2002). Guthion was detected in 8 out of 321 raw water samples at a mean concentration of 0.077 μg/L and a maximum concentration of 0.144 μg/L. Guthion was detected in 5 out of 225 finished drinking water samples at a mean concentration of 0.059 μg/L and a maximum concentration of 0.114 μg/L. The main metabolite in chlorinated waters, gutoxon was detected in 1 out of 316 raw water samples at a concentration of 0.263 μg/L and in 4 out of 219 finished drinking water samples at a mean concentration of 0.18 μg/L and a maximum concentration of 0.26 μg/L (EPA 2002). Guthion or the oxon metabolite was only detected in drinking water samples collected from Missouri, New York, Oklahoma, and South Carolina. Guthion and its metabolite were not detected in raw or treated water samples obtained from California, Indiana, Louisiana, North Carolina, Ohio, Pennsylvania, South Dakota, or Texas (EPA 2002).

Due to spray drift, runoff, and erosion of treated soils, guthion is frequently detected in surface waters adjacent to farming areas where it has been applied as an insecticide. The U.S. Geological Survey maintains and operates The National Water Quality Assessment Program (NAWQA) database, which frequently updates groundwater and surface water monitoring data for various pesticides, including guthion, in >50 major river basins in the United States. Data from 1991, 1994, and 1997 indicated that guthion was detected in 1.31% of 1,800 water samples collected at 75 streams near agricultural locations in the United States. The maximum concentration of guthion in these streams was reported as 0.5 μg/L (USGS 2003).

Guthion was detected in 13 out of 142 surface water samples collected at four sites in the San Joaquin River Basin at a maximum concentration of 0.39 μg/L (Dubrovsky et al. 2000). Guthion levels at these sites tended to spike during the summer months, coinciding with the agricultural season and then decrease during the winter. For example, guthion levels in Orestimba Creek in the San Joaquin River Basin fluctuated between 0.1 and 0.2 μg/L from June to September 1992, and then decreased sharply from November 1992 to May 1993, before increasing to 0.4 μg/L in June 1993 (USGS 1999). Guthion was detected in 64 out of 98 surface water samples at a maximum concentration of 0.523 μg/L obtained from various sites in a heavy apple growing region along the Yakima River Basin, Washington during the period of May 1999 through January 2000 (USGS 2001). The study authors noted that concentrations of guthion exceeded its chronic-toxicity guideline for the protection of aquatic life in 50% of the samples. Monitoring data from the Washington State Department of Agriculture from April to October 2004, reported guthion levels of 0.013–0.042 μg/L (4 positive detections out of 31 samples) in the Sulphur Creek Wasteway near its confluence with the Yakima River (Burke et al. 2005). In addition, it was detected in 4 out of 45 samples obtained from Spring Creek near its confluence with the Yakima River at levels ranging from 0.014 to 0.023 μg/L (Burke et al. 2005). Sampling data from April to December 2003 in Sulphur Creek had 11 positive detections of guthion with a maximum concentration of 0.025 μg/L (Anderson et al. 2004). Guthion was detected in 0.5% of the surface water samples collected in two streams located in Oregon, at a maximum concentration of 0.171 μg/L (Hoffman et al. 2000). Guthion was detected in 12 out of 29 surface water samples obtained from a creek (Crab Creek Lateral) that feeds into Royal Lake, in Central Washington State during March 1993 to May 1994 sampling (Gruber and Munn 1998). The maximum observed concentration was 0.2 μg/L. It was reported that most of the flow of water into Crab Creek Lateral is the result of excess irrigation water that enters the canal from agricultural drains and groundwater discharges. An analysis of pesticide residues in U.S. groundwater and streams from 1992 to 2001 was recently summarized by analyzing data in the NAWQA database (USGS 2006a). Guthion exceeded benchmark levels (0.18 μg/L for acute fish toxicity, 0.36 μg/L for chronic fish toxicity, 0.08 μg/L for acute invertebrate toxicity, 0.16 μg/L for chronic invertebrate toxicity) for aquatic life in approximately 20% of the agricultural streams and 10% of the urban streams included in the sampling program (USGS 2006a). Guthion was detected in 11 water samples at a maximum concentration of 0.034 μg/L collected from four major irrigation return-flow drainage basins, in agricultural areas of Washington State from July 2002 through October 2004 (USGS 2006b).

The EPA Office of Water maintains the STOrage and RETrieval (STORET) database, which contains data for guthion in surface water throughout the United States. Information from this database is of limited value because it is difficult to determine the purpose and circumstances of the studies contained in the database. According to the studies included in STORET, only 15 out of 1,123 samples at 653 sites had detectable levels of guthion in the United States over a multi-year period (EPA 1999a). These data are summarized in Table 6-4. Data maintained in the STORET database for 2005–2006 did not include any positive detections of guthion in water samples (EPA 2006k).

6.4.3 Sediment and Soil

Guthion was detected at levels of <0.1 mg/kg in surface soils (upper 6 inches) of Marengo, Alabama (Albright et al. 1974). Soil samples collected from 48 homes of agricultural families in eastern Washington State had mean guthion levels of 60 μg/kg (range: not detected to 814 μg/kg), while soil samples collected from 11 homes of nonagricultural families had no detectable levels of guthion (detection limit 32 μg/kg) (Simcox et al. 1995). For the homes of the agricultural families, a positive correlation was observed between guthion levels in the soil and household dust, and the proximity to nearby apple orchards (Simcox et al. 1995). In a study of 49 randomly chosen agrichemical facilities located throughout the state of Illinois, guthion was detected in soil samples at 5 of the 10 sites that processed, used, or handled it (Krapac et al. 1995). The mean, median, and range of guthion concentrations in the soil samples at these five sites were reported as 148, 110, and 45–878 μg/kg, respectively.

Data maintained in the STORET database for 2005–2006 included seven detections of guthion in sediment samples obtained from Escambia County, Florida at concentrations ranging from 6.6 to 23 μg/kg (EPA 2006k).

Table 6-4. Guthion Levels in Surface Water from the STORET Database

Water body	Number of samples	Number of detects	Number of sites	Maximum concentration (μg/L)	Years
Canals	289	3	63	0.01	1974–1993
Estuaries	185	2	162	3	1969–1997
Lakes	406	1	242	0.01	1974–1996
Oceans	16	0	6	Not applicable	1980–1985
Reservoirs	91	9	57	0.01	1975–1995
Springs	136	0	123	Not applicable	1987–1996

Source: EPA 1999a

6.4.4 Other Environmental Media

Guthion has frequently been detected in foods in the United States, primarily in fruits and vegetables. In 2002, the EPA Office of Pesticides Programs published a cumulative risk assessment that evaluated the cumulative dietary risk due to the use of organophosphate pesticides on food crops (EPA 2002). In this assessment, residue monitoring data collected by the U.S. Department of Agriculture's Pesticide Data Program (USDA-PDP) supplemented with information from the FDA Center for Food Safety and Applied Nutrition (FDA/CFSAN) were analyzed. Residue data were collected on approximately 44 food commodities monitored by PDP between the years 1994 and 2000. The data pertaining to guthion are summarized in Table 6-5. In general, guthion was detected at levels below 1 ppm in most food items, although a single maximum occurrence of 1.9 ppm was reported for guthion in pears (EPA 2002). Data from the FDA Total Diet Study Market Basket Survey from 1991 to 2001 indicated that guthion was detected in 15 out of 320 food items in the surveys. It was most frequently detected in red apples (32 detections with a maximum concentration of 0.19 ppm) and pears (29 detections with a maximum concentration of 0.227 ppm), but was also detected in nonfruit or vegetable items including cheddar cheese and blueberry muffins (FDA 2003).

Over a 5-year period (1991–1995), guthion was detected in 295 out of 2,338 fruits and vegetables analyzed in a market basket survey in Canada (Ripley et al. 2000). Only two other pesticides (dithiocarbamate and captan) were detected more frequently in fruits and vegetables than guthion in this Canadian survey.

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

The general population is primarily exposed to guthion through the ingestion of food items, although minor exposure may occur from inhalation of ambient air and ingestion of drinking water. Urinary metabolites that are reflective of exposure to guthion were measured as a part of the National Health and Nutrition Examination Surveys (NHANES) (CDC 2005). These dialkyl phosphate metabolites are not specific to guthion, but their detection indicates the possibility of exposure to guthion and several other organophosphate pesticides. Dialkyl phosphates may also be present in the environment from the degradation of these pesticides. Therefore, in addition to reflecting exposure to guthion or other organophosphate pesticides, the presence of the metabolites in a person's urine may also reflect exposure to the metabolite itself (CDC 2005). Six dialkyl phosphates were measured in the most recent NHANES and the results for the three compounds that are known metabolites of guthion, dimethyl phosphate (DMP), dimethyl thiophosphate (DMTP), and dimethyl dithiophosphate (DMDTP) are reported in

Table 6-5. Guthion Residues in Various Foods from 1994 to 2000

Food item	Number analyzed	Number of detections	Average concentration (ppm)[a]	Maximum concentration (ppm)
Apple juice	1,554	81	4.9×10^{-5}	0.008
Apples	2,471	1,228	0.028	0.46
Apples (single serving)	377	220	0.022	0.77
Bananas	1,126	0	0	0
Broccoli	678	0	0	0
Cantaloupe	1,640	0	0	0
Carrots	2,072	0	0	0
Celery	176	0	0	0
Cherries	275	163	0.027	0.44
Corn Syrup	423	0	0	0
Cucumbers	1,467	0	0	0
Grape juice	1,379	0	0	0
Grapes	2,625	41	0.00119	0.47
Green beans (canned)	853	0	0	0
Green beans (fresh)	1,897	9	1.2×10^{-4}	0.051
Green beans (frozen)	729	3	1.2×10^{-4}	0.038
Lettuce	1,616	0	0	0
Milk	1,892	0	0	0
Nectarines	345	48	0.0049	0.2
Oats (bran)	45	0	0	0
Oats (rolled)	287	0	0	0
Orange juice	1,392	0	0	0
Oranges	2,636	2	3.5×10^{-5}	0.073
Peaches (canned)	754	1	7.0×10^{-5}	0.053
Peaches (fresh)	1,623	511	0.022	0.72
Peaches (single serving)	534	218	0.0214	0.65
Pears (canned)	737	0	0	0
Pears (fresh)	1,773	1,039	0.0503	1.9
Pears (single serving)	696	275	0.0318	0.87
Pineapples	104	0	0	0
Potatoes	1,770	0	0	0
Poultry (adipose tissue)	476	0	0	0
Poultry (liver)	479	0	0	0
Poultry (muscle)	145	0	0	0
Soybean grain	748	0	0	0
Spinach (canned)	863	0	0	0
Spinach (fresh)	1,639	4	4.46×10^{-4}	0.4
Spinach (frozen)	714	1	1.8×10^{-5}	0.013
Strawberries (fresh)	1,768	2	1.52×10^{-4}	0.2
Strawberries (frozen)	155	3	0.001781	0.2

Table 6-5. Guthion Residues in Various Foods from 1994 to 2000

Food item	Number analyzed	Number of detections	Average concentration (ppm)[a]	Maximum concentration (ppm)
Straw bell peppers	1,468	9	1.9×10^{-4}	0.11
Sweet corn (canned)	652	0	0	0
Sweet corn (fresh)	19	0	0	0
Sweet corn (frozen)	635	0	0	0
Sweet peas (canned)	746	0	0	0
Sweet peas (fresh)	9	0	0	0
Sweet peas (frozen)	703	0	0	0
Sweet potatoes	1,559	0	0	0
Tomatoes (canned)	737	5	8.4×10^{-5}	0.013
Tomatoes (fresh)	1,960	31	0.000748	0.71
Wheat	940	3	7.0×10^{-5}	0.022
Winter squash (fresh)	1,216	0	0	0
Winter squash (frozen)	470	0	0	0

[a] Nondetects were counted as zero in calculating the average.

Source: EPA 2002

Tables 6-6, 6-7, and 6-8. A general reduction in urinary levels of these metabolites has been observed from the 1999–2000 survey data with the levels from the 2001–2002 data.

The average daily dietary intake (AVDI) of guthion categorized by age and gender groups is shown in Table 6-9. These data were developed from the FDA Total Diet Study (TDS), which collects foods from several regional and metropolitan areas that are representative of the total diet of the U.S. population. These dietary intake values are lower than several toxicological benchmark values including the World Health Organization (WHO) Acceptable Daily Intake (ADI) of 5 μg/kg/day and the EPA Office of Pesticides Program's acute oral reference value of 3 μg/kg/day (EPA 1999b, 2001b; Fenske et al. 2000a).

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 Section 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).

Similar to adults, children are primarily exposed to guthion through the ingestion of foods. The dietary AVDI of guthion has been reported as 0.069–0.083 μg/kg-body weight/day for 6–11-month-old infants and 0.022–0.031 μg/kg-body weight/day for 2-year-old toddlers (Gunderson 1988, 1995). No measurements have been made of guthion in amniotic fluid, meconium, cord blood, neonatal blood, or any other tissues that may indicate prenatal exposure. No data have been reported on the levels of guthion in breast milk. The metabolite DMP was detected in 1 out of 20 postpartum meconium samples obtained from newborn infants at the New York Presbyterian Hospital (Whyatt and Barr 2001). The metabolites DMTP and DMDTP were not detected. A study conducted in Rio Negro, Argentina analyzed the acetylcholinesterase activity in placenta tissue and plasma of 200 pregnant females (Souza et al. 2005). Guthion is a frequently used pesticide in this heavy apple and pear growing region. A correlation

Table 6-6. Selected Percentile Urine Concentrations (µg/L) of DMP in the U.S. Population from 1999 to 2002[a]

Group	Percentile				Sample size
	50th	75th	90th	95th	
Age 6 and older					
1999–2000	0.740	2.80	7.90	13.0	1,949
2001–2002	<LOD	3.25	8.22	13.4	2,519
6–11 Years					
1999–2000	1.00	4.40	10.0	21.0	471
2001–2002	0.970	5.03	12.2	18.2	576
12–19 Years					
1999–2000	0.650	3.80	9.90	22.0	664
2001–2002	0.670	4.27	9.27	14.6	822
20–59 Years					
1999–2000	0.680	2.60	6.50	9.70	814
2001–2002	<LOD	2.93	6.89	11.5	1,121
Males					
1999–2000	0.650	2.80	7.90	18.0	952
2001–2002	<LOD	3.40	8.22	12.6	1,187
Females					
1999–2000	0.780	2.80	7.60	10.0	997
2001–2002	<LOD	3.05	8.34	13.7	1,332
Mexican Americans					
1999–2000	1.00	3.80	9.50	15.0	672
2001–2002	0.660	3.22	9.38	14.4	678
Non-Hispanic blacks					
1999–2000	0.980	3.60	8.90	21.0	509
2001–2002	0.910	5.45	11.5	19.4	695
Non-Hispanic whites					
1999–2000	<LOD	2.90	7.90	10.0	595
2001–2002	<LOD	3.01	7.39	12.3	948

[a] The proportion of the results below the LOD was too high to calculate geometric means for DMP.

DMP = dimethyl phosphate; LOD = limit of detection

Source: CDC 2005

Table 6-7. Geometric Mean and Selected Percentile Urine Concentrations (µg/L) of DMTP in the U.S. Population from 1999 to 2002

Group	Geometric mean	Percentile 50th	75th	90th	95th	Sample size
Age 6 and older						
1999–2000	1.82	2.70	10.0	38.0	46.0	1,948
2001–2002	[a]	0.450	4.02	16.2	32.6	2,518
6–11 Years						
1999–2000	2.72	4.10	20.0	40.0	62.0	471
2001–2002	[a]	1.44	8.33	28.2	45.7	575
12–19 Years						
1999–2000	2.53	3.60	16.0	37.0	69.0	664
2001–2002	[a]	1.03	4.83	20.8	33.9	822
20–59 Years						
1999–2000	1.59	2.20	9.10	38.0	38.0	813
2001–2002	[a]	<LOD	3.32	13.6	29.5	1,121
Males						
1999–2000	2.10	3.40	13.0	38.0	41.0	952
2001–2002	[a]	0.610	4.21	18.3	30.4	1,187
Females						
1999–2000	1.59	2.00	9.70	38.0	52.0	996
2001–2002	[a]	<LOD	3.76	15.9	34.3	1,331
Mexican Americans						
1999–2000	1.79	2.00	10.0	38.0	130	671
2001–2002	[a]	<LOD	3.74	15.1	35.2	678
Non-Hispanic blacks						
1999–2000	2.13	3.60	11.0	37.0	39.0	509
2001–2002	[a]	1.25	5.54	20.6	42.2	695
Non-Hispanic whites						
1999–2000	1.77	2.60	11.0	38.0	45.0	595
2001–2002	[a]	<LOD	3.99	17.0	32.6	947

[a] The proportion of the results below the LOD was too high to calculate a geometric mean.

DMTP = dimethyl thiophosphate; LOD = limit of detection

Source: CDC 2005

Table 6-8. Selected Percentile Urine Concentrations (μg/L) of DMDTP in the U.S. Population from 1999 to 2002[a]

Group	Percentile				Sample size
	50th	75th	90th	95th	
Age 6 and older					
1999–2000	<LOD	2.30	12.0	19.0	1,949
2001–2002	<LOD	0.890	0.49	4.95	2,518
6–11 Years					
1999–2000	0.730	4.30	16.0	32.0	471
2001–2002	<LOD	1.30	3.53	7.33	575
12–19 Years					
1999–2000	<LOD	2.20	12.0	19.0	664
2001–2002	<LOD	0.810	2.51	4.63	821
20–59 Years					
1999–2000	<LOD	2.10	10.0	16.0	814
2001–2002	<LOD	0.840	2.32	4.90	1,122
Males					
1999–2000	0.110	2.30	16.0	18.0	952
2001–2002	<LOD	0.840	2.40	5.13	1,187
Females					
1999–2000	<LOD	2.10	10.0	20.0	997
2001–2002	<LOD	0.950	2.52	5.10	1,331
Mexican Americans					
1999–2000	0.240	1.80	5.70	12.0	672
2001–2002	<LOD	0.960	2.66	4.47	678
Non-Hispanic blacks					
1999–2000	0.330	3.20	14.0	18.0	509
2001–2002	<LOD	0.750	2.11	4.38	695
Non-Hispanic whites					
1999–2000	<LOD	2.00	13.0	20.0	595
2001–2002	<LOD	0.940	2.49	5.74	947

[a] The proportion of the results below the LOD was too high to calculate geometric means for DMDTP.

DMDTP = dimethyl dithiophosphate; LOD = limit of detection

Source: CDC 2005

Table 6-9. Dietary Average Daily Intake of Guthion (µg/kg/day)

	1982–1984[a]	1986–1991[b]
6–11 Months	0.0069	0.0083
2 Years	0.022	0.0311
14–16 Years (female)	0.0048	0.0061
14–16 Years (male)	0.0050	0.0073
25–30 Years (female)	0.0046	0.0061
25B30 Years (male)	0.0033	0.0044
60B65 Years (female)	0.0062	0.0079
60B65 Years (male)	0.0051	0.0064

[a] Gunderson 1988
[b] Gunderson 1995

between acetylcholinesterase activity in plasma and timing of pesticide applications was observed. An 18% reduction in maternal plasma acetylcholinesterase activity was observed during the pesticide application months of November–February as compared to samples collected in non-application months (March–October); however, a slight increase in activity was observed in placenta tissue during the pesticide application months.

Nondietary ingestion may be an important exposure pathway in agricultural areas, where guthion is used as an insecticide. The tendency of young children to ingest soil, either intentionally through pica or unintentionally through hand-to-mouth activity, is well documented. These behavioral traits can result in ingestion of guthion present in soil and dust. Young children often play on the ground or on carpets and this will increase the likelihood of dermal exposure and inhalation of contaminated particles from soil, household dust, and treated surfaces. The exposure of young children to organophosphate pesticides, including guthion, in an agricultural community in central Washington was studied by collecting spot urine and hand wipe samples from a group of 109 children aged 6 months to 6 years during the pesticide spraying months of May–July (Lu et al. 2000). Participants included 62 agricultural families (49 applicators and 13 farm workers) and 14 reference families in which no family member was employed in occupations requiring contact with pesticides, and the residence was located at least one quarter mile away from any pesticide treated orchard. There were 72, 19, and 18 children of pesticide applicators, farm workers, and reference families, respectively. The median urinary levels of the dimethyl metabolites DMTP and DMDTP were 0.05 μg/mL in the children of the agricultural families and 0.01 μg/mL in the children of reference families (Lu et al. 2000). Approximately 67% of the urine samples collected from the children of farm applicator and farm workers contained detectable levels of DMTP, while 53% of the urine samples collected from the children of reference families contained detectable levels. Wipes obtained from the hands of the children indicated that detectable levels of guthion were present in approximately 13% of the children's hands from agricultural families; while none of the children from the reference families had detectable levels of guthion in hand wipe samples. Additional exposure to guthion may also arise from the clothing or personal items of adults that are employed in pesticide application or other farm work. For instance, the mean guthion level on the surface of work boots in the agricultural families was 0.03 μg/cm^2 and the mean level on the steering wheel of the family vehicle was 0.001 μg/cm^2 (Lu et al. 2000). Guthion was not detected on personal clothing items or in the vehicles of the 14 reference families.

Urinary levels of dialkyl phosphates were monitored in children residing in agricultural communities in Washington State over a 21-month period (Koch et al. 2002). Although several pesticides are used in this area, the authors reported that guthion is the most frequently applied insecticide in the agricultural region studied. The overall geometric mean urinary level of combined DMP, DMTP, and DMDTP was reported as 0.080 µmols/L for all samples collected over this 21-month period. The highest levels of dialkyl phosphates measured in the urine coincided with the orchard spraying season (geometric mean of 0.096 µmols/L), while the lowest levels were observed during the winter nonspraying months (geometric mean of 0.072 µmols/L). A similar study was conducted by measuring the combined levels of DMP, DMTP, and DMDTP in the urine of children from 218 farm workers households in agricultural communities of Washington State (Curl et al. 2002). DMP, DMTP, and DMDTP were identified in 19, 88, and 45%, respectively, of the 211 urine samples collected and the geometric mean concentration of the combined dialkyl phosphate metabolites was 0.09 µmols/L (Curl et al. 2002). Urine samples collected from 88 children in central Washington State indicated that DMTP was quantified more often in the urine of children of pesticide applicators when compared with reference children (Loewenherz et al. 1997). Detectable levels of DMTP were observed in 47% of the urine samples obtained from the children of pesticide applicators, compared to 27% for the reference group. The median DMTP concentration in the urine of the agricultural children was 0.021 µg/mL (0.15 µmols/L) compared to 0.005 µg/mL (0.035 µmols/L) for the reference children (Loewenherz et al. 1997).

Aggregate dose estimates for guthion and phosmet were calculated for children in an agricultural community in the state of Washington (Fenske et al. 2000a). These estimates were generated from the urinary metabolite concentrations of DMTP and DMDTP in 109 children up to 6 years of age residing in this community. Since guthion and phosmet were the organophosphates most often used in this area, it was assumed that the dialkyl phosphate metabolites measured in urine samples were due exclusively to these two pesticides. The mean (± standard deviation) creatinine adjusted dose for the children of agricultural families was 3.5 (±4.2) µg/kg/day during the 6–8-week spraying season (May—July), as compared to 2.0 (±3.1) µg/kg/day for reference children. The mean creatinine adjusted single day dose was 3.7 (±5.9) µg/kg/day for children of agricultural families as compared to 2.1±4.1 µg/kg/day for reference children (Fenske et al. 2000a). Although the large standard deviation suggests a high degree of variability, these estimated intakes are much larger than the FDA estimated dietary intakes of the general population (Gunderson 1988, 1995) and are of the same order of magnitude as the WHO ADI of 5 µg/kg/day.

These findings suggest that children in agricultural communities where guthion is used as an insecticide are potentially exposed more frequently and to higher levels than children in the general population through nondietary exposure pathways.

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Pesticide applicators, farm workers, and people living in close proximity to agricultural areas such as apple and cherry orchards where guthion is frequently used are potentially exposed to higher levels of guthion than the general population. In addition to ingestion of contaminated foods, inhalation and dermal exposures to farm workers and their families are considerably higher than for the general population. Household dust and soil samples were collected from 59 residences in Washington State (Simcox et al. 1995). The households were classified as 26 farming, 22 farm workers, and 11 nonfarming families. The majority of agricultural families inhabited homes within 200 feet of an operating apple or pear orchard. The mean concentration of guthion in household dust of the 48 agricultural households was 1.870 µg/g (0.170–11.270 µg/g range), while the mean concentration in household dust of the nonagricultural homes was 0.330 µg/g (0.134–0.816 µg/g range) (Simcox et al. 1995). Household dust samples were collected from the homes of 96 farm workers and 24 apple growers in Oregon to assess potential exposure of migrant farm workers to organophosphate pesticides in this community (McCauley et al. 2001). Mean levels of guthion in dust samples were 1.45 µg/g in the homes of farm workers and 1.64 µg/g in the homes of growers. The mean guthion level in household dust samples collected from the homes of 62 agricultural families in central Washington State was 1.94 µg/g (Lu et al. 2000). The mean guthion level in household dust obtained from the homes of 14 reference families was 0.29 µg/g. This represents an approximate 7-fold greater guthion exposure level in the homes of agricultural workers as compared to nonagricultural families. Levels of guthion in household dust samples were also shown to be highest among residences closest to the pesticide-treated apple orchards (Lu et al. 2000). Guthion was detected in 133 out of 156 household dust samples and 165 out of 190 vehicle dust samples from agricultural workers in Washington State (Curl et al. 2002). The geometric mean concentration in house dust was reported as 0.53 µg/g (14.9 µg/g maximum level), while the geometric mean concentration of guthion in vehicle dust was reported as 0.75 µg/g (38.3 µg/g maximum level).

The urinary levels of DMP, DMTP, and DMDTP were measured in 11 workers engaged in thinning and picking practices in a peach orchard that had been sprayed 20 days prior with chlorpyrifos methyl and guthion (Aprea et al. 1994). The average level of the three metabolites in the urine of workers wearing different types of protective equipment in the peach orchard during work operations ranged from approximately 470 to 940 nmols/g creatinine, depending on the type of equipment used. A separate subject not wearing gloves or a mask during work operations had a mean urinary level of nearly 4,000 nmols/g creatinine for the three metabolites (Aprea et al. 1994). A control group of

99 nonoccupationally exposed persons had a mean urinary level of approximately 200 nmols/g creatine. The authors concluded that the main route of guthion absorption to the workers was from dermal exposure, but that respiratory exposure was also significant (Aprea et al. 1994).

Dermal absorption of guthion in humans and animals have been demonstrated in several studies. The amount of guthion absorbed through human skin was studied by applying 500–6,000 µg guthion to the forehead of volunteers and monitoring the level of DMTP excreted in urine over a 72-hour period (Franklin et al. 1986). The results of this pilot study are summarized in Table 6-10. The authors concluded that approximately 30–40% of the applied dose was absorbed in humans, as compared to nearly 100% in rats and rabbits (Franklin et al. 1986). This estimate is somewhat higher than other estimates from experimental data. As summarized in a risk characterization document developed by the California EPA, guthion was applied topically to the forearms of six volunteers in isopropyl alcohol at 2.6 and 9.2 $\mu g/cm^2$ or in an aqueous suspension of Guthion 25 WP at 4.7 $\mu g/cm^2$ for an exposure period of 8 hours (California EPA 2004). Blood samples were collected up to 5 days postapplication and urine and feces were collected for 13 days postapplication. The dermal absorption was measured as the sum of the radioactivity in the urine, feces, and tape stripping. The dermal absorption ranged from 21.5% for aqueous suspension of the wettable powder to 27.8% for the technical-grade material applied in isopropyl alcohol at the lower concentration. Another study summarized in this document estimated the dermal absorption of guthion in an acetone-based solution as 16% (California EPA 2004). Absorption of guthion applied to the skin of male rats continued following application with subsequent washing with water, and the amount of absorption was observed to be dose-dependent (Zendzian 2003).

In conclusion, agricultural workers and their families are likely to be exposed more frequently, and to higher levels of guthion than the general population if they are involved with procedures such as spraying, harvesting, or thinning of crops in which guthion has been applied as an insecticide. In addition to ingesting food items containing guthion, agricultural workers and their families may be subject to additional dermal and inhalation exposures from dusts, soils, and personal items such as clothing contaminated with guthion.

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 guthion is available. Where adequate information is not

Table 6-10. Excretion of DMTP Following the Dermal Application of Guthion to Volunteers

Dose (µg/person)	Cumulative DMTP total in urine (µg)			DMTP/guthion[a]
	24 hours	48 hours	72 hours	
500	54	76	85	17
1,000	96	130	152	15
2,000	56	90	119	6
4,000	154	267	404	10
6,000	153	284	323	5

[a] Cumulative amount of DMTP excreted divided by amount of guthion applied, multiplied by 100.

DMTP = dimethyl thiophosphate

Source: Franklin et al. 1986

available, ATSDR, in conjunction with 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 guthion.

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

6.8.1 Identification of Data Needs

Physical and Chemical Properties. The physical and chemical properties of guthion are sufficiently well defined to allow assessments of the environmental fate of this compound to be made (Gawlik et al. 1998; Hansch et al. 1995; Suntio et al. 1988; Tomlin 2003). Some physical and chemical properties of guthion that are not relevant to environmental fate are lacking. Knowledge of these properties, such as flashpoint and flammability limits, would be useful for workers involved in the manufacture, use, or clean-up of guthion; however, no data need is identified at this time.

Production, Import/Export, Use, Release, and Disposal. According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit substance release and off-site transfer information to the EPA. The TRI, which contains this information for 2005, became available in May of 2007. This database is updated yearly and should provide a list of industrial production facilities and emissions.

There are no data available regarding the production, import, or export volumes of guthion. Many of guthion’s uses were cancelled by the EPA in 2001 and all remaining uses are scheduled to be cancelled by 2012. Incineration and alkaline hydrolysis are the two methods employed to dispose of guthion. No data need is identified at this time.

Environmental Fate. Sufficient data are available to characterize the environmental fate of guthion. When applied as an insecticide, guthion adsorbs strongly to soil surfaces and is degraded in the environment by a combination of biotic and abiotic reactions. It may enter nearby water bodies through spray drift, runoff, and erosion of treated soils where it is expected to partition to suspended solids and sediment. Data are available regarding the rate of hydrolysis (EPA 1999a; Lartiges and Garrigues 1995), photolysis (EPA 1999a; Lartiges and Garrigues 1995), biodegradation (Diaz Diaz et al. 1995; EPA 1999a), foliar dissipation (Granovsky et al. 1996), and terrestrial field dissipation for guthion (EPA 1999a). The important transport and partitioning properties of guthion have also been studied including adsorption/desorption in soil (EPA 1999a; Gawlik et al. 1998) and runoff potential following its application (EPA 1999a). No data needs are identified at this time.

Bioavailability from Environmental Media. Guthion is absorbed following both oral and dermal exposures (Fakhr et al. 1996; Franklin et al. 1986). No experimental studies were located regarding the bioavailability of guthion from contaminated soil, water, and air; therefore, data are needed regarding the bioavailability of guthion from soil and other environmental media.

Food Chain Bioaccumulation. Data are needed regarding the food chain bioaccumulation of guthion. An estimated BCF value of 26 was calculated for guthion; however, experimentally determined BCF values in fathead minnows were significantly larger than this estimated value (Knuth et al. 2000). A lipid-corrected BCF value of approximately 3,000 was observed in minnows. When these lipid corrected BCF values were adjusted to whole-body BCF values, the data were more consistent with the estimated value. More experimental bioconcentration data on different species of fish along with depuration kinetics are required to assess this end point.

Exposure Levels in Environmental Media. Reliable monitoring data for the levels of guthion in contaminated media at hazardous waste sites are needed so that the information obtained on levels of guthion in the environment can be used in combination with the known body burden of guthion to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

Monitoring data for guthion are available in air (Coupe et al. 2000; Foreman et al. 2000; Majewski et al. 2000), water (California EPA 1995; EPA 1992b, 1999a, 2002; Gruber and Munn 1998; Kolpin et al. 2000; USGS 2006a, 2006b), soil (Krapac et al. 1995; Simcox et al. 1995), and food (EPA 2002; FDA 2003; Ripley et al. 2000). Additional data are required regarding the levels of guthion in fish and animal tissues. Continued monitoring of guthion residues in foods and other environmental media, particularly in agricultural fields where it is extensively used or from hazardous waste sites, would be helpful for further assessing the potential for human exposure.

Exposure Levels in Humans. Direct monitoring data of guthion in humans is rare since its biological half-life is short. Metabolites such as DMP, DMTP, and DMDTP have been monitored in urine of individuals (Aprea et al. 1994; CDC 2005; Fenske et al. 2000a; Loewenherz et al. 1997; Lu et al. 2000). These metabolites are not specific to guthion, but indicate potential exposure to several organophosphate pesticides. Continued monitoring data, particularly chronic low-level exposure data for humans in the vicinity of agricultural locations where it is frequently used or hazardous waste sites, are necessary.

This information is necessary for assessing the need to conduct health studies on these populations.

Exposures of Children. Similar to adults, exposure measurements for the guthion metabolites in children are available (CDC 2005; Fenske et al. 2000a; Koch et al. 2002; Loewenherz et al. 1997; Lu et al. 2000). Children in the general population are exposed to guthion primarily through the dietary ingestion of contaminated food items. A unique exposure pathway exists for children of agricultural families that reside near farms or orchards where guthion is used. Potential exposure to guthion from parents clothing, family automobiles, and personal items exists (Lu et al. 2000). Since guthion has also been detected in soil and dust samples in or around homes where it is used, common play activities on the ground or pica may result in exposure for these children. Continued monitoring data is necessary for assessing the need to conduct health studies on exposed children. In addition, a data need exists for the levels of guthion or metabolites in breast milk.

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

Exposure Registries. No exposure registries for guthion were located. This substance is not currently one of the compounds for which a sub-registry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for sub-registries 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 this substance.

6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2006) 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. Researchers at the University of California, Department of Entomology (R.I. Krieger, principal investigator) are studying the dermal transfer of guthion and other pesticides from treated turf and other environmental surfaces to children. Researchers at the Washington State University Food and Environmental Quality Laboratory are measuring the atmospheric deposition and spray drift characteristics of guthion applied to apple orchards in Washington State.