6. POTENTIAL FOR HUMAN EXPOSURE

6.1 OVERVIEW

Atrazine has been identified in at least 20 of the 1,636 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 atrazine is not known. The frequency for these sites within the United States can be seen in Figure 6-1. Of these sites, all 20 are located within the United States and none are located in the Commonwealth of Puerto Rico (not shown). Significant amounts of atrazine are also released during manufacture, formulation, transport, storage, and disposal (see Section 6.2 below).

Atrazine is an extensively-used, broad leaf herbicide, and virtually the entire production volume is released to the environment as a result of agricultural and other weed-control practices. In its recommended applications, atrazine is used as a preemergence and postemergence herbicide for corn, sorghum, sugarcane, macadamia nuts, and other crops, as well as in conifer reforestation, and as a nonspecific herbicide for the treatment of fallow soil and highway right-of-ways. Therefore, most environmental atrazine releases will occur as a result of its intended usage. There are no known natural sources of atrazine.

While atrazine is a widely-used herbicide, it is not available to the general public, as it is classified as a restricted-use pesticide (RUP). RUPs are, by law, only for retail sale to and use by certified applicators or persons under their direct supervision, and only for those purposes covered by the applicator's certification. Atrazine received this classification on January 23, 1990 (Fishel 2000).

The normal agricultural use of atrazine will result in some loss or transport from the soil into the atmosphere, where it may later undergo deposition back to soils or into bodies of water. Some atmospheric release of atrazine will also occur as a result of its formulation, manufacture, and disposal. It may also enter air by loss of applied herbicide before it reaches the soil, and by particle distribution of dusts that contain atrazine. Volatilization of atrazine following application to fields has been measured to be up to 14% of the applied amount. Once in the air, atrazine will exist in both the particulate and vapor phases due to its vapor pressure. These forms will influence how atrazine is transported or later deposited on to terrestrial or aquatic environments.

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

Atrazine's concentration in air will vary with application season; measured concentrations have ranged from just above the detection limit (~0.03 ng/m^3) to more typical concentrations of 0.20–0.32 µg/m^3. As a result of atrazine's vapor and particulate phase distribution, and climate patterns during and following application, it can be transported in the atmosphere significant distances from its application area; it has been detected as far as 100–300 km (62–186 miles) from the closest application area. While in the atmosphere, it has not been observed to undergo direct photolytic degradation. However, vapor-phase atrazine can be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals. Particulate-phase atrazine will be removed from the atmosphere by wet and dry deposition; atrazine is commonly found in rainwater in the seasons following agricultural applications.

Atrazine may also be transported from where it is applied to soils by runoff into surface water and percolation into groundwater. Atrazine tends to persist in surface and groundwater, with a moderate tendency to bind to sediments. Slow or no biodegradation occurs in surface water or groundwater environments, respectively. When it is degraded in aquatic systems, hydroxyatrazine, deethylatrazine, and deisopropylatrazine are the major products formed by chemical and biological processes. Depending on the availability of sunlight, oxygen, microorganisms, and plants, the half-life of atrazine in water tends to be longer than 6 months; in some cases, no degradation of atrazine has been observed in aquatic systems. This lack of degradability is one reason that atrazine is commonly observed in surface waters and well-water drinking water supplies. This long residence time in surface waters indicates that it may have the opportunity to enter the food chain. Atrazine has a slight to moderate tendency to bioconcentrate in microorganisms, algae, aquatic invertebrates, worms, snails, or fish. It is only slightly toxic or nontoxic to fish and other aquatic invertebrates, and has been shown to have short-term effects on fish behavior.

Atrazine is not very persistent to moderately persistent in surface soils, with reported half-lives commonly ranging from 14 to 109 days. However, it has been observed to persist in some soils for up to 4 years, and there are instances where no biodegradation has been observed in some subsurface soils or in aquifer materials. It can be detected in soils where it has been applied as a pesticide, as well as in soils that have been impacted by runoff or by atmospheric deposition. In soils, it may undergo abiotic hydrolysis to hydroxyatrazine, but this occurs very slowly unless dissolved organic matter is present or the soils are extremely acidic. It is generally biodegraded by soil microorganisms to hydroxyatrazine, deethylatrazine, or deisopropylatrazine, with subsequent metabolism to cyanuric acid. This may be followed by relatively complete degradation to CO_2 (mineralization) within 20 weeks. Anaerobic biodegradation occurs very

slowly, with half-lives of over 200 days. This half-life may include some abiotic degradation since hydroxyatrazine was the only observed degradation product. Atrazine, however, has been reported to degrade more quickly in anaerobic soil under strongly reducing conditions.

Even though atrazine is a widely used pesticide for corn, sugarcane, macadamia nuts, sorghum, and other crops, very few atrazine residues have been found in food analyses conducted by the FDA and the USDA from 1987 to the present. Atrazine concentration was very low (0.001–0.028 μg/g) in the few samples where it was detected. In contrast, atrazine has been detected in many drinking water well samples, especially in the areas where it is used on corn crops. These data suggest that most members of the general population have little or no exposure to atrazine from foods. People who use products that contain atrazine, however, such as those involved in farming, or during its manufacture, or in other uses where atrazine has been approved, are more likely to be exposed to atrazine. It has been estimated that approximately 1,000 industrial workers are exposed to atrazine per year (NIOSH 1989). People who live in regions where atrazine is used may be exposed to atrazine in drinking water that is obtained from wells. In studies of drinking water wells in midwestern states, atrazine was found in up to 41% of the municipal wells tested (Kolpin et al. 1997a). In Maine, it was detected in 31% of the drinking water wells (Bushway et al. 1992). Nationwide, the EPA estimated that atrazine was present in 1,570 community water source (CWS) wells and in 70,800 rural domestic wells (EPA 1990a).

6.2 RELEASES TO THE ENVIRONMENT

All atrazine is commercially produced for the control of broad-leaf and other weeds, in formulations designed for preemergence or postemergence of crops, or for weed control in nonspecific applications, such as the treatment of fallow land or highway right-of-ways. Therefore, all manufactured atrazine is expected to be released to the environment, primarily soils, during these activities. Release data generated for the Toxics Release Inventory (TRI) (e.g., Table 6-1) also details release, but should be used with caution because only certain types of facilities are required to report, and data from these reports do not represent an exhaustive list of all commercial releases. It should be noted that for atrazine, since it is one of the most widely-used agricultural herbicides in the United States, the TRI data represent only a small fraction of the environmental release.

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

Reported amounts released in pounds per year[a]								
State[b]	Number of facilities	Air[c]	Water	Under-ground injection	Land	Total on-site release[d]	Total off-site release[e]	Total on and off-site release
AL	1	672	11	0	0	683	0	683
AR	2	500	5	0	0	505	250	755
FL	4	250	No data	0	510,160	510,410	187,372	697,782
GA	1	0	No data	0	0	0	0	0
IA	3	3,428	0	0	0	3,428	12,933	16,361
IL	2	521	No data	0	0	521	500	1,021
LA	1	18,816	668	535	0	20,019	13,628	33,647
MI	1	10	0	0	0	10	0	10
MO	2	158	0	0	0	158	0	158
MS	1	500	250	0	0	750	0	750
NE	4	7	0	0	0	7	38	45
OH	2	10	0	0	0	10	755	765
Total	24	24,872	934	535	510,160	536,501	215,476	751,977

Source: TRI01 2003

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

Table 6-1 shows the 2001 TRI releases of atrazine from manufacturing or processing facilities to different environmental compartments. Most of the atrazine released to the environment from these facilities was released to soils. Of the 24 facilities producing or processing atrazine, 15 facilities reported that a total of 24,872 pounds (11,282 kg) were released to the air, four facilities reported releasing 934 pounds (423 kg) to surface water, one facility reported release of 535 pounds (243 kg) by underground injection, and three facilities reported release of 510,160 pounds (231,405 kg) to land (TRI01 2003). The releases to land represented 95% of the total releases of atrazine (TRI01 2003). All three sites reporting releases to land are located in Florida. Two of those sites were owned by one company, and the combined amount released to land from those two sites was over half (51%; 260,160 pounds; 118,007 kg) of the total atrazine released to land. These high releases in Florida were a result of Standard Industrial Code activities related to sugar cane and sugar beet processing, and activities related to disposal and refuse systems (# 4953).

Release of atrazine from these facilities has changed from year to year since the TRI listing for atrazine began in 1995 (TRI01 2003). Reported air releases have ranged from a low of 20,946 pounds (9,501 kg) released in 1999 to a high of 35,119 pounds (15,930 kg) released in 1997. Surface water releases have ranged from a low of 934 pounds (423 kg) released in 2001 to a high of 2,756 pounds (1,250 kg) released in 1998. Land releases have fluctuated more, with the lowest amount (388,928 pounds; 176,417 kg) being released in 1997 and the highest amount (637,036 pounds; 288,958 kg) being released in the year that reporting began (1995). It should be emphasized, however, that TRI does not report agriculture-related releases, and that atrazine is one of the most widely used herbicides in the United States. For example, in 1981, for the state of New York alone, an estimated 2,495,800 pounds (1,132,087 kg) of atrazine were applied to soils for herbicidal use (Walker and Porter 1990).

The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

In addition to releases related to agricultural or other weed treatment usage, atrazine has been identified in several environmental compartments including surface water, groundwater, soil and sediment collected at 20 of the 1,636 current or former NPL hazardous waste sites (HazDat 2003).

6.2.1 Air

Atrazine has been detected in the atmosphere, both nearby and distant from areas where it has been applied as a pesticide. In addition to detecting atrazine in the atmosphere in the vicinity of and distant from where it is used in agricultural or other broad-leaf weed control activities, atrazine has also been detected in the air near 14 of 22 manufacturing or processing facilities that report atrazine releases (TRI01 2003). The total amount of atrazine released to the atmosphere by these sites was 33,807 pounds (15,335 kg). In contrast to detecting atrazine in the atmosphere in relation to TRI-reported manufacture, processing, or agricultural practices, atrazine was not identified in air samples near the 20 sites collected from the 1,636 NPL hazardous waste sites where it was detected in some environmental media (HazDat 2003).

When atrazine was measured in the air near its agricultural or other applications, in some cases, it was only been found in the atmosphere during the first month following the application of the herbicide to crops (Elling et al. 1987). In other cases, it was found at 4 months (Chevreuil et al. 1996) to 8 months afterwards (Wu 1981). The manner in which atrazine is applied to the fields may influence its entry (i.e., volatilization) to the atmosphere. Cumulative volatilization of atrazine from conventionally- tilled fields was equal to 14% of the amount applied, but only 9% of the total applied amount was volatilized from no-till fields (Weinhold and Gish 1994). Glotfelty et al. (1989) measured the volatilization of atrazine and other pesticides from moist and dry soils, and found that 2.4% of the applied atrazine had volatilized after 21 days. The total mass of atrazine that was volatilized to the atmosphere can be calculated using these percentages and the quantities used on croplands. The highest reported amount of atrazine used on croplands was 90,340,000 pounds in 1976 in the United States (Section 5.3; Ribaudo and Bouzaher 1994). If one assumes that 2.4% of this volatilized, then the amount of atrazine was distributed to the atmosphere was 2,168,160 pounds. If one assumes that 14% was volatilized, then 12,647,600 pounds was distributed to the atmosphere. The lowest amount of atrazine reported was in 1964, where 10,837,000 pounds of atrazine was used on all crops (Ribaudo and Bouzaher 1994). In this case, 2.4% volatilization would represent 260,088 pounds being distributed to the atmosphere; 14% volatilization would represent 1,517,180 pounds being distributed. For comparison, in 1997, 74,560,407 pounds of atrazine was applied to crops in the United States (NCFAP 2000). If one assumes that 2.4% of this volatilized, then this represents 1,789,450 pounds of atrazine being distributed to the atmosphere. If one assumes that 14% was volatilized, then this represents 10,438,457 pounds. In all cases, the amounts distributed to the atmosphere represent significantly more than the amounts distributed to the atmosphere as a result of manufacture or disposal.

6.2.2 Water

According to the TRI, 1,034 pounds (469 kg) of atrazine were released to water from four facilities that manufacture or process atrazine (TRI01 2003). Atrazine has been identified in groundwater and surface water at 12 and 9 of the 1,636 NPL hazardous waste sites, respectively, where it was detected in some environmental media (HazDat 2003). Atrazine may also be found in surface and groundwater as a result of its formulation, manufacture, use and disposal. In addition, atrazine has been found in surface water and groundwater, as well as in drinking water wells, as a result of its application to crop fields as a preemergence herbicide. It has been detected in groundwater more frequently than any other pesticide (Dorfler et al. 1997; Koskinen and Clay 1997).

As a result of surface runoff from agricultural application and deposition by precipitation, atrazine is commonly found in streams, rivers, and lakes (Gaynor et al. 1995), salt marshes and their sediments (Meakins et al. 1995), and the ocean (Bester and Huhnerfuss 1993). It is found in higher concentrations in waters near high usage areas, such as the corn-belt in the upper midwest in the United States (Thurman et al. 1991).

6.2.3 Soil

Atrazine is widely used as a preemergence herbicide, and has been broadly applied to agricultural soils. It is commonly found in agricultural soils following application for several weeks to a few years. Atrazine may also be found in soils as a result of its formulation, manufacture, and disposal. According to the TRI, 501,732 pounds (227,582 kg) of atrazine were released to soil from four facilities that manufacture or process atrazine (TRI01 2003). Atrazine has been identified in soil and sediments in 7 and 6 of the 1,636 NPL hazardous waste sites, respectively, where it was detected in some environmental media (HazDat 2003). According to Ribaudo and Bousahar (1994) 49,553,000 pounds (22,477,093 kg) of atrazine were used on 45,333,000 acres (18,346,014 hectares) of corn in the United States in 1993; the maximum reported usage was in 1976, when 90,340,000 pounds (40,839,154 kg) of atrazine were used in all agricultural applications.

6.3 ENVIRONMENTAL FATE

This section refers to the transport and partitioning of 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine, the major component in technical-grade atrazine and the primary component of most atrazine-containing herbicides. Please see Section 4.1, Chemical Identity, for a discussion of the few impurities documented in technical-grade atrazine. It is reported to only contain three classes of impurities, dichlorotriazines, hydroxytriazines, and tris(alkyl)aminotriazines. Little information is available on the fate of these impurities (HSDB 2001).

6.3.1 Transport and Partitioning

Atrazine has been detected in the atmosphere, both nearby and distant from areas where it has been applied as a pesticide. Based on its vapor pressure, atrazine will exist in both the particulate and vapor phases in the atmosphere, but should tend to exist more in the particulate phase than in the vapor phase. However, atrazine has been shown to volatilize from agricultural soils in the United States (Glotfelty et al. 1989; Weinhold and Gish 1994), and has been found in the vapor phase in the atmosphere (Chevreuil et al. 1996), in association with fog (Glotfelty et al. 1987) and rainwater (Bester and Huhnerfuss 1993; Trevisan et al. 1993; Wu 1981). In some monitoring studies, atrazine was found in the atmosphere only during the first month following the application of the herbicide to crops (Elling et al. 1987); in other cases, it was found 4 months (Chevreuil et al. 1996) to 8 months after application (Wu 1981).

The manner in which atrazine is applied to the fields may influence its volatilization to the atmosphere. Cumulative volatilization of atrazine from conventionally tilled fields was equal to 14% of the amount applied, but only 9% of the total applied was volatilized from no-till fields (Weinhold and Gish 1994). Air concentrations of atrazine vary with application season; concentrations usually range from just above the detection limit of ~0.03 ng/m^3 to more typical concentrations of 0.20–0.32 µg/m^3 (Trochimowicz et al. 2001).

Atrazine can be detected significant distances (100–300 km; 62–186 miles) away from the closest application area (Thurman and Cromwell 2000; Thurman et al. 1995) as a result of atmospheric transport. Atrazine is removed from the atmosphere by both precipitation and dry deposition, but precipitation is thought to be the primary mechanism for atrazine removal (Thurman and Cromwell 2000). In a study conducted in Germany, it was detected in 22–29% of precipitation samples collected over a 2-year period

(Siebers et al. 1994), with average concentrations ranging from 0.044 to 0.105 µg/L. In a study conducted on rainfall in the state of Iowa, 39% of 325 rainwater samples contained atrazine at concentrations ranging from 0.1 to 40 µg/L (Koskinen and Clay 1997). The average and median amounts detected were 0.91 and 0.34 µg/L, respectively. Atrazine concentrations ranged from <5 to 380 ng/L (median=50 ng/L) in rainfall collected from a rural site near Paris, France. In an urban collection area in Paris, the range was <5–400 ng/L (median also 50 ng/L) (Cheveuil et al. 1996). In a study of airborne dust samples from South Dakota, 50% of the collected samples contained atrazine or other triazine herbicides; concentrations of the total triazine herbicides in these dust samples ranged from 0.29 to 0.76 µg/g.

Atrazine can leach through the soil column and contaminate groundwater. When atrazine is deposited into aquatic matrices, some is expected to remain in the water column and some is expected to partition into the sediments. Atrazine has a measured log octanol/water partition coefficient (log K_{ow}) of 2.6–2.71 (Brown and Flagg 1981; Hansch et al. 1995) and has a solubility in water of 34.7 mg/L (Ward and Weber 1968). Atrazine has been shown to be relatively mobile in soils (Redondo et al. 1997; Southwick et al. 1995). In a silt loam soil, atrazine migrated almost as quickly at the conservative bromide tracer (Starr and Glotfelty 1990). Due to its high mobility, atrazine is commonly found in groundwater and as a contaminant of drinking water wells. In a study of groundwater sites in Iowa, atrazine was found in up to 41% of the 106 municipal wells tested in midwestern states (Kolpin et al. 1997a).

Experimentally-measured adsorption coefficients (log K_{oc}) for atrazine have been determined and range from 1.96 to 3.38. However, studies have not demonstrated a relationship between the measured log K_{oc} and organic matter content (Dousset et al. 1994; Koskinen and Rochette 1996; Weber 1991). This suggests that the adsorption of atrazine to soil is influenced by processes other than interactions with soil organic matter, such as interactions with clays or coatings on quartz minerals. Koskinen and Rochette (1996) observed this type of disparity between the K_{oc} of atrazine and soil moisture variations, and suggested that different types of interactions occur under different moisture regimes. Changes in the test conditions allowed for different interactions to occur between the atrazine and the clay minerals and soil organic matter. Wetting and drying cycles also enhanced the sequestration of atrazine in soil samples compared to those in which atrazine was exposed to continuous moisture (Kottler et al. 2001).

Following application to crop soils, most atrazine is found at the highest concentrations in the upper layers of soil, as a result of sorption (Koskinen and Clay 1997). Atrazine's rate of transport is dependent on many soil factors including the soil type, the amount of water that is applied to the soil, the presence of

crop residues, and the types of any fertilizers used. Soil pH may also affect the transport of atrazine. Atrazine sorption to soils increased with pH decreasing from 7.5 to 5.6 in a study of 10 Danish aquifer materials (Madsen et al. 2000). However, its mobility through soils, especially through macropores, has been demonstrated. In comparison to two other triazine herbicides (simazine and ametryn), atrazine was shown to be the most mobile in subtropical soils (Wang et al. 1996). Furthermore, the active ingredient of the applied herbicide moves more rapidly through soils than its breakdown products (Tasli et al. 1996). Its transport has been shown to occur along roots or through earthworm burrows (Koskinen and Clay 1997). In soils where mobile colloids are present, atrazine may be adsorbed and carried through preferential flow-paths in the soil and finally into groundwater (Sprague et al. 2000).

Atrazine transport varies from soil to soil, and laboratory experiments have suggested both significant and restricted movement of atrazine. In a study that examined of the effects of soil type, especially of sandy soils, on mobility, atrazine's mobility was higher in soils with higher hydraulic conductivities and less sorptive capacity (Wietersen et al. 1993). In contrast, in a soil column study, only small amounts of atrazine (~3%) were reported to leach in a sand or silt loam soil to a depth of 60–100 cm; most remained in the upper 15 cm of the soil (Koskinen and Clay 1997).

6.3.2 Transformation and Degradation

Atrazine is degraded slowly in most environments, whether by biological or chemical (e.g., photolysis) processes. Klint et al. (1993) observed no biodegradation of atrazine in groundwater or in groundwater combined with aquifer sediment systems, over a period of 539 days under anaerobic conditions. Anearobic degradation, however, was shown to occur under strongly reducing conditions by Seybold et al. (2001). Abiotic degradation of atrazine occurs by hydrolysis to hyrdroxyatrazine (2-hydroxy-4-ethyl-amino-6-isopropylamino-*s*-triazine), but this process is also very slow. Widmer et al. (1993) observed almost no hydrolysis of atrazine in typical groundwater over 19 weeks. No direct photolytic degradation has been detected in natural systems (Curran et al. 1992; Pelizzetti et al. 1990), but it is expected to undergo oxidation in the atmosphere in the presence of hydroxyl radicals, with an estimated half-life of 14 hours.

When atrazine is biodegraded, it is primarily biodegraded by dealkylation, where some organisms remove the ethyl moiety, forming deethylatrazine (2-chloro-4-amino-6-isopropylamino-*s*-triazine). Other microorganisms are effective at removing the isopropyl group, forming 2-chloro-4-ethylamino-6-amino-*s*-

triazine. Still others are capable of degrading atrazine through the formation of hydroxyatrazine. All of these transformations may lead to the complete degradation of atrazine, but this is not always observed. It is somewhat persistent in natural environments, as biodegradation slowly occurs in soils (Mandelbaum et al. 1993), sediments (Seybold et al. 1999), and surface waters (Feakin et al. 1994). In some cases, rather that being biodegraded, atrazine residues become incorporated into unextractable residues (Seybold et al. 1999), which are considered to be less bioavailable than the free parent or metabolite compounds. Seybold et al. (1999) showed that 2 years after exposure to atrazine, <2% of extractable atrazine or its metabolites remained in two different soil-based sediments.

6.3.2.1 Air

Atrazine has not been observed to undergo direct photolytic degradation in the atmosphere (Pelizzetti et al. 1990). It is, however, expected to undergo degradation in the atmosphere in the presence of hydroxyl radicals in the atmosphere. The half-life of atrazine is estimated to be 14 hours for a hydroxyl radical concentration of 5.0×10^5 OH^-/cm^3. It should be stated however, that this rate of photodegradation is expected for vapor-phase atrazine only; particulate-phase atrazine would not be expected to undergo photodegradation at this rate. This difference in atmospheric photodegradation rates is important since atrazine can be transported significant distances in the atmosphere. If atrazine existed primarily in the vapor phase in the atmosphere, a half-life of 14 hours would be expected to remove most of it from the atmosphere prior to deposition.

6.3.2.2 Water

Atrazine degradation in surface waters is slow, and its biodegradation in surface waters has not been demonstrably observed. It has been shown to have long residence times in the water column of lakes and streams, with half-lives >200 days. Photolysis of atrazine has not been demonstrated in water, unless substantial amounts of dissolved organic matter of acidic conditions are present (Curran et al. 1992; Penuela and Barcelo 2000). Atrazine degradation in surface waters appears to be primarily due to abiotic hydrolysis (Feakin et al. 1994), and losses from small streams were also best explained by an abiotic mechanism (Kolpin and Kalkhoff 1993). Biodegradation of atrazine has not been shown to occur in natural waters under aerobic conditions. Furthermore, no significant atrazine degradation has been observed under anaerobic conditions. Adrian and Suflita (1994) observed no anaerobic degradation of atrazine in aquifer slurries. No degradation of atrazine was observed in an alluvial gravel aquifer over a

distance of 90 m and a period of 49 hours. Atrazine concentrations were significantly reduced in batch tests over a period of 194 days; however, analysis suggests that the degradation is from chemical reduction and not biodegradation (Pang and Close 1999). Atrazine was degraded in the aqueous phase above anaerobic soil with a half-life of 86 days, under strongly reducing conditions (Seybold et al. 2001). Biodegradation has been shown only to occur when pure cultures of atrazine degraders are isolated from water or soil samples and grown in the laboratory; the activities of these organisms in the laboratory, however, have little or no relevance to natural aquatic biodegradation processes. Therefore, it appears that biodegradative losses of atrazine in aquatic systems are negligible.

6.3.2.3 Sediment and Soil

In a review of the fate of factors that affect atrazine persistence in soils of the United States, Kosikinen and Clay (1997) found that its removal half-life in soils ranged from 14 to 109 days, with a median half-life of 39 days. They acquired these half-lives from 15 field persistence studies of atrazine. It should be noted that in these determinations, disappearance of atrazine includes all mechanisms of removal including biodegradation, photolysis, volatilization, percolation into groundwater, and irreversible binding to soils. Most disappearance patterns were biphasic, with relatively faster disappearance occurring over the first few months following application, with slower disappearance kinetics occurring over the subsequent time period. Factors that were shown to affect the length of the half-life included soil type and the concentration of applied atrazine. Tillage practices had a slight influence on degradation, but this was not significant (Koskinen and Clay 1997).

Atrazine biodegradation in soils is relatively slow, with half-lives ranging from 4 to 57 weeks (Best and Weber 1974; Mandelbaum et al. 1993). It is somewhat persistent in natural environments, but biodegradation slowly occurs in soils (Mandelbaum et al. 1993) and sediments (Seybold et al. 1999). Atrazine disappearance has been demonstrated in soils, but its microbial mineralization is not commonly observed in soils. In a study of surface soils, Sinclair and Lee (1992) noted that even with long-term (12 years) exposure of soils to atrazine on treated roadsides, the indigenous microbes did not acclimate to atrazine, as atrazine was not biodegraded in soils collected from these sites. After 161 days, 80% of the added atrazine had disappeared from the surface soils, but there were no differences between the sterile and nonsterile soil treatments. Furthermore, atrazine was completely stable in all of the subsurface samples studied. Kruger et al. (1997) observed similar trends. No complete biodegradation (mineralization) of atrazine was observed in either saturated or unsaturated soils, at different depths over a

period of 120 days. Moderate amounts (5.8–66%) of the atrazine remained in the soils, depending on the amount of water saturation or depth of the soil. However, these amounts were no different from the amounts measured in sterile control soils, strongly suggesting that abiotic mechanisms were responsible for the degradation or loss of atrazine. Although no complete biodegradation was observed, degradation products were observed, including deethylatrazine and deisopropylatrazine. Half-lives calculated from the disappearance of atrazine ranged from 36 to 204 days in either the sterile or nonsterile soil.

Rodriguez and Harkin (1997) found slight, but insignificant degradation of atrazine in two different subsoils slurries over a period of over 270 days. Half-lives for atrazine were calculated to be 5.2 and 1.4 years in the different slurries. In a soil microcosm study, Dousset et al. (1997) observed no mineralization of atrazine in three different soils. Half-lives for the parent compound were calculated to be 66–105 days. In another study of the fate of atrazine in agricultural soils, atrazine had a half-life of 25–40 days in three nonsterile soils. In the control (sterilized) soils, atrazine had similar half-lives of 37–134 days (Qiao et al. 1996). Atrazine biodegradation was also measured in forest and grassland soils (Entry and Emmingham 1996). The authors found that after 30 days of incubation, atrazine was not degraded in the organic layer of grassland soils, and that only 1.2% degradation was observed in a mineral soil. More degradation was observed in the forest soils, with maximum amounts of mineralization (4.3%) observed in soil collected from a coniferous forest.

While little atrazine mineralization has been documented in soils, some studies have noted the formation of chlorinated derivatives of atrazine (Koskinen and Clay 1997; Kruger et al. 1997). Rodriquez and Harkin (1997) noted the formation of significant amounts of deethylatrazine (17.6%) and smaller amounts of deisopropylatrazine (2.7%) after 270 days in soils. Dousset et al. (1997) noted the formation of s-triazine derivatives following atrazine application, and 33–43% of these became incorporated into nonextractable soil residues.

Only a few studies have noted significant biodegradation of atrazine in soils. In a laboratory study, atrazine degradation in some soils was found to be concentration-dependent, with almost complete biodegradation of atrazine occurring within 20 weeks in a clay loam soil, at concentrations ranging from 5 to 5,000 mg/kg (Gan et al. 1996). By contrast, in a sandy loam soil, biodegradation was faster for the lower concentrations of atrazine in comparison to higher concentrations. At the highest concentration studied (5,000 mg/kg), however, no atrazine mineralization was observed in this soil. The authors did not supply a mechanistic explanation for the observed differences. Another study showed considerable and rapid atrazine mineralization in soil collected from the surface and subsurface of an agricultural site in

Ohio (Radosevich et al. 1996). In this study, relatively complete mineralization was observed within 50 days in soils collected from an area that has been historically exposed to atrazine. Atrazine mineralization half-lives in selected soils ranged from 3.4 to 43 days for surface soils, and from 17 to 43 days for subsurface samples. Mineralization was more rapid in soils collected near the surface as compared to those collected at depths >5 meters. The authors noted that some samples collected from this area (9 of 14) showed no mineralization of atrazine. The spatial variability in observed atrazine degradation led the authors to conclude that atrazine persistence in some soils was due to a lack of atrazine degraders in the soil, and not due to lack of appropriate nutrients or to unfavorable sorptive conditions (Radosevich et al. 1996). Ames and Hoyle (1999) argue that comparisons of bulk sediment parameters are useless for predicting biodegradation potential without knowledge of the distribution of atrazine-degrading microorganisms. In a study of atrazine biodegradation in 44 soil samples from a 3 ha contaminated agricultural chemical dealership, only samples from the southeastern corner showed biodegradation of atrazine. In most of these samples, atrazine was biodegraded to concentrations below detectable levels in 40 and 80 days, which was not predicted by sediment parameters.

Microorganisms (or groups of microorganisms) have been found that can degrade atrazine (Mandelbaum et al. 1993; Radosevich et al. 1995, 1996; Struthers et al. 1998; Wenk et al. 1998); the first isolation of a bacterium that could completely degrade atrazine, however, was not reported until 1995 (Radosevich et al. 1995). These strains have shown the capacity to degrade atrazine when added to soils contaminated with the pesticide, and have been developed for bioremediation applications in both soils and sediments. Crawford et al. (1998) showed that an atrazine-degrading bacterium could degrade atrazine under denitrifying conditions, and suggested that atrazine degradation occurred in indigenous lake sediments. However, no significant degradation occurred (approximately 0.5%) under these conditions. Therefore, while some bacterial strains can degrade atrazine in remediation applications, their activities should not be considered relevant to the environmental persistence of atrazine in soil. Atrazine has not been observed to undergo photolytic degradation in soils (Curran et al. 1992), nor abiotic hydrolysis in neutral pH groundwater when dissolved organic matter is present (Widmer et al. 1993). Atrazine was degraded in anaerobic soil with a half-life of 38 days under strongly reducing conditions (Seybold et al. 2001).

6.3.2.4 Other Media

The accumulation, persistence, and effects of atrazine have been measured in several other environmental media. These include oceans (Bester and Huhnerfuss 1993) and waste water treatment systems

(Nsabimana et al. 1996), as well as in animals (i.e., fish, tadpoles, invertebrates; see below) that inhabit freshwater environments.

In the ocean, atrazine has been measured at concentrations ranging from 1 to 100 ng/L (Bester and Huhnerfuss 1993), indicating that atrazine can be transported to the ocean, and that degradation during transport and residence there may not be rapid. In waste water treatment systems, atrazine has been shown to have little overall effect on treatment processes, but did tend to decrease microbial biomass.

6.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

6.4.1 Air

Atrazine has been observed in most air samples where it has been sought. In some cases, it has been detected only in rainwater. In a study conducted in Italy of the atmospheric fate of 12 different pesticides, atrazine was one of the most frequently detected herbicides in rainwater. In this experiment, atrazine was observed in 10 samples out of 146 collected (Trevisan et al. 1993). In the 10 rainwater samples that contained atrazine, its concentrations ranged from 0.15 to 1.99 μg/L, with a median concentration of 0.88 μg/L. These amounts fluctuated with the season, such that the highest concentrations were found around the month of June, following the earlier spring-time application of the herbicide to crops (Trevisan et al. 1993). These seasonal-based observations were similar to those of Bester and Huhnerfuss (1993) who noted higher atrazine concentration in rainwater during the months following application of the herbicide. In France, air concentrations of atrazine fluctuated depending on application season; concentrations usually ranged from just above the detection limit of ~0.03 ng/m^3 to more typical concentrations of 0.20–0.32 μg/m^3 in regions in and around Paris, France (Trochimowicz et al. 2001). In a study of airborne dust samples from South Dakota, 50% of the collected samples contained atrazine or other triazine herbicides; concentrations of the total triazine herbicides in these dust samples ranged from 0.29 to 0.76 μg/g (Muller et al. 1997).

Atrazine was detected in 70–96% of weekly rainwater samples taken from urban and agricultural sites in Mississippi, Missouri, and Iowa (Majewski et al. 2000). Positive weekly air samples ranged from 30 to 75% at urban sites and from 50 to 83% at agricultural sites (Foreman et al. 2000). Atrazine was detected in 76% of rainwater samples and 35% of air samples at a background site in Eagle Harbor, Michigan, indicating the potential for atrazine to undergo long-range transport. The concentration of atrazine in precipitation over Lake Michigan was found to be 0.10–0.40 μg/L during a study involving over

600 atmospheric samples (gas, particulate, and precipitation) from July 1994 to September 1995. Annual loading into Lake Michigan was found to be $1.04x10^3$ kg/year (Miller et al. 2000). Another study reported that the average atrazine concentrations monitored in the five Great Lakes from 1991 to 1995 are well below the U.S. Safe Drinking Water Act Minimum Contaminant Level of 3 µg/L and the Canadian Aquatic Life Criteria of 2 µg/L (Tierney et al. 1999).

The difference between atrazine concentrations in urban and rural air was emphasized in a study that compared rainwater and air samples from the urban area of Jackson, Mississippi with samples from the agricultural region of Rolling Forks, Mississippi (Coupe et al. 2000). Atrazine was detected in 69% of rainwater samples from Jackson with a median concentration of 0.006 µg/L compared to 75% of rainwater samples from Rolling Forks with a median concentration of 0.02 µg/L. Atrazine was detected in 29% of particulate samples from Jackson with a median concentration below the detection limit compared to 67% of particulate samples from Rolling Forks with a median concentration of 0.058 ng/L. Atrazine was detected in 42% of gas samples from Rolling Forks with a median concentration below the detection limit. Atrazine was not detected in gas samples taken from Jackson.

6.4.2 Water

In a study of atrazine distribution to several bodies of water in the northern midwestern United States, atrazine was consistently detected in samples collected before crop planting, shortly thereafter, and at harvest time. Atrazine concentrations, however, fluctuated considerably. It was detected in 91% of surface water (river and stream) samples that were collected before crops were planted, and in 98% of water samples collected after the crops were planted. Following the growth season (at harvest), it was detected in 76% of the collected water samples. In a similar set of monitoring studies in Canada, atrazine was detected in 80% of the agricultural watershed streams that were sampled. In this study, concentrations were measured in streams in 11 different agricultural watersheds (Frank et al. 1982). The highest concentration that was detected was 33 µg/L, with the average concentrations ranging from 1.1 to 1.6 µg/L. Mississippi River samples collected at Baton Rouge, Louisiana from 1991 to 1997 contained atrazine with a median concentration of ~0.45 µg/L (Clark et al. 1999). The flux of atrazine in the Mississippi River at Baton Rouge, Louisiana from January 1996 through September 1997 was 963 metric tons. All 129 samples taken from 75 Midwestern streams and rivers in 1998 contained atrazine (Battaglin et al. 2000). The median and maximum concentrations were 3.97 and 224 µg/L, respectively. Atrazine was detected at 14 out of 25 groundwater sites in the same region. Median and maximum concentrations

were 0.010 and 0.410 µg/L, respectively. The USGS analyzed 2,485 sites from 20 of the nation's major hydrologic basins for pesticides from 1992 to 1996 during the USGS National Water Quality Assessment Program (Kolpin et al. 2000). Atrazine was found in 30% of the samples with a maximum concentration of 4.20 µg/L. Atrazine was detected with a concentration of 5.06 µg/L in samples from flood waters of the Nishnabotna River in Southwest Iowa (USGS 2000). This flood took place in June 1998, shortly after chemical application associated with planting of crops.

Concentrations of atrazine in surface waters that are impacted by agricultural use tend to fluctuate with the season, with the highest atrazine concentrations being observed in the weeks and months following application of the herbicide (Albanis et al. 1998; Battaglin and Goolsby 1999). Since atrazine is a preemergence herbicide, these detections would occur prior to planting and shortly thereafter. For example, atrazine was detected in 91% of 55 surface water (river and stream) samples that were collected before crops were planted, and in 98% of 132 water samples collected within 2 weeks of crop planting. Following the growth season (at harvest), it was detected in only 76% of 145 of the water samples collected (Thurman et al. 1991). These observations show that atrazine was consistently detected in these water samples early in the growth season, but it should be noted that the concentrations of atrazine fluctuated considerably. The samples collected after the crops were planted contained an order of magnitude higher concentrations (median concentration ≈4 µg/L) than either the preplanting or harvest samples, which had median concentrations of approximately 0.4 µg/L. In a similar set of monitoring studies in Canada, atrazine was detected in 80% of the agricultural watershed streams that were sampled. In this study, concentrations were measured in streams in 11 different agricultural watersheds (Frank et al. 1982). The highest concentration that was detected was 33 µg/L, with the average concentrations ranging from 1.1 to 1.6 µg/L.

To address the amounts of atrazine that reach streams as a result of agricultural runoff, studies have been conducted to investigate the concentrations of atrazine in surface runoff following application (Gaynor et al. 1995). Atrazine concentrations in surface runoff were greatest following application of the herbicide to the fields, and it was found that the concentrations varied according to the agricultural practice used. The highest maximum amount of atrazine observed in surface runoff, 700 µg/L, occurred when the fields were managed by a no-till cultivation practice; lower maximum surface runoff concentrations were observed (400 µg/L) when conventional tillage was used. It should be noted that in the receiving streams, atrazine concentrations were about 10-fold lower than surface runoff concentrations. This difference was a result of sorptive and other losses that occurred prior to the surface runoff reaching the surface bodies of water (Gaynor et al. 1995), not simply dilution into the larger amount of receiving waters. It should be

noted that the amounts of atrazine lost by volatilization from no-tillage fields vs. conventional tillage fields contrast with runoff observations. Following application of atrazine to conventional tillage fields, up to 14% was volatilized. Less atrazine volatilization (9%) was observed following application to no-tillage fields (Wienhold and Gish 1994). Leaching after a heavy rainfall was reported to hinder the volatilization of atrazine in freshly tilled soil (Rice et al. 2002). Atrazine loss due to volatile fluxes was 7.5% after 20 days, with 59% of the loss occurring within 4 days of treatment.

Based on a 5-year National Survey of Pesticides in Drinking Water Wells (NPS), the EPA estimated that atrazine was present in 1,570 CWS wells nationwide (EPA 1990a). Due to the statistical nature of the estimation calculation used, the estimates range from a low of 420 to a high of 2,701 CWS wells. The EPA also estimated that there are 70,800 rural domestic wells contaminated with atrazine (estimates range from a low of 13,300 to a high of 214,000) (EPA 1990a). The estimates assume only that the concentration of atrazine would be above the limits of detection (0.12 µg/L) used in the survey. However, the maximum atrazine concentration detected in a CWS well was 0.92 µg/L; the maximum concentration detected in a rural domestic well was 7.0 µg/L (EPA 1990a). A more recent report found maximum seasonal and annual average concentrations of atrazine plus chlorinated metabolites to be 61.6 ppb and 18.9 ppb, respectively, during a 1993–1998 monitoring program of 13 CWS in the United States that use surface water (EPA 2002a). Atrazine is generally found at higher concentrations in CWS that use surface water sources compared to those that use groundwater sources.

In a study in Maine, atrazine was detected in 18 out of 58 (31%) drinking water wells. Most wells contained <0.6 µg/L atrazine, but two contained atrazine at concentrations >3 µg/L (Bushway et al. 1992). In a study of groundwater underneath irrigated farmland in central Nebraska used primarily for growing corn, atrazine was detected in all of the 14 wells tested (Spalding et al. 1980). Concentrations in these wells ranged from 0.06 to 3.12 µg/L, with an average concentration of 0.75 µg/L (Spalding et al. 1980). In a study of groundwater sites in Iowa, atrazine was found in 41% of the 106 municipal wells tested in 1995 (Kolpin et al. 1997a), in 4.4% of 686 rural wells examined during 1988–1989, and in 12% of 355 groundwater monitoring wells during 1982–1987. In a broader study of groundwater quality in Iowa, 209 (19.5%) of 1,485 wells tested contained atrazine at concentrations above 0.1 µg/L (Kolpin et al. 1997b). The amounts of atrazine found in wells in Iowa remained relatively constant from 1982 to 1985, reflecting the constant usage of atrazine in Iowa agriculture (Kolpin et al. 1997b). In contrast, a survey of 103 randomly-chosen farmstead wells in Kansas found that only 4 were contaminated by atrazine (Steichen et al. 1988). The concentrations detected were higher, and changed with season. The highest detected atrazine concentration was 7.4 µg/L during the winter. When these wells were sampled again

during May or June, an even higher maximum concentration of atrazine, 40 µg/L, was detected. It was proposed that the higher levels observed in the spring months reflected usage patterns that had occurred prior to sampling. It should be noted that this study had a relatively high detection limit for atrazine of 1.2 µg/L (Steichen et al. 1988).

Atrazine is also commonly found in other bodies of water such as man-made canals (Miles and Pfeuffer 1997), estuaries (Wu 1981), and lakes (Muller et al. 1997). Triazine herbicides, including atrazine, were the most commonly-detected pesticides in a 5-year monitoring study of 27 water sampling stations in canals found in southern Florida. In these canals, atrazine represented 37% of all pesticide detections, and was present in the water at concentrations up to 18 µg/L (Miles and Pfeuffer 1997). As in other studies (e.g., surface runoff monitoring studies), atrazine was detected primarily in the months around application in the spring. Similar observations of atrazine concentration fluctuations were noted for the Rhode River estuary in Maryland. Wu (1981) measured atrazine concentrations in this estuary for over 2 years. However, atrazine was present in the estuary waters all year, and ranged in concentration from 0.006 to 0.19 µg/L. In a longer-term (5-year) study of atrazine in three Swiss lakes, Muller et al. (1997) found that the amount of atrazine was very dependent upon the amount of rainfall that occurred during the application period, and transport to the lake was dominated by rainfall, not surface runoff. This was suggested by the observation that while the three lakes had very different cachement areas and hydraulic properties, atrazine deposition was relatively uniform in each lake receiving similar amounts of rainfall. It was estimated that total inputs into the lakes reflected 0.5% of the soil-applied atrazine in a dry application period to up to 2% of the soil-applied atrazine during a wet (rainy) application period (Muller et al. 1997).

6.4.3 Sediment and Soil

Atrazine residues vary in soils, depending on usage and exposure to climatic patterns that may lead to atrazine deposition. In soils, atrazine has been found at high concentrations resulting from applications. Atrazine is moderately persistent in surface soils. Its concentrations in soils have been shown to slowly decline over a periods of 12 months in surface soils, from 0.83 µg/g 6 days following application of 1.1 kg/ha, to 0.5 µg/g 2 months following application, to 0.08 µg/g 12 months following application (Frank and Sirons 1985). Similar trends of disappearance were observed when it was applied at concentrations of 2.2 or 3.3 kg/ha (Frank and Sirons 1985); in all cases, concentrations had dropped by approximately 90% over a period of 1 year. Regardless of the application rate, atrazine had a half-life of

approximately 3.3 months in the soils (Frank and Sirons 1985). The initial atrazine concentration in sandy loam samples taken from a plot sewn with maize was 0.670 mg/kg (Konda and Pasztor 2001). This concentration decreased to 0.376 mg/kg (56.2%) after 14 days and 0.242 mg/kg (36.1%) after 28 days. Only 1.37% of the initial concentration of atrazine was detected after 140 days. Atrazine levels were also monitored in agricultural soil plots in Minnesota, which showed slightly different trends. Levels of atrazine in the surface layers (0–10 cm depth) of a sandy loam soil dissipated (disappeared or leached) over the 13-month study (Gan et al. 1996). In one test in this study, a high concentration of atrazine, representing a spill event (6.3 g/kg), was applied to the soil and its concentrations monitored over 13 months. At the end of the monitoring period, only 0.13 g/kg remained in this soil layer. When normal application concentrations (7.2 mg/kg) were applied to the same soil, however, dissipation was slower, and after 13 months, concentrations had only been reduced to 2.3 mg/kg. Similar trends were observed in a clay loam soil, but dissipation was somewhat faster and more uniform in the clay loam soil as compared to the sandy loam soil (Gan et al. 1996). A complimentary study examined atrazine dissipation in three agricultural soils from Germany. In all soils, atrazine levels decreased in a relatively linear fashion from approximately 5.5 to 1 mg/kg over 110 days. There was very little difference in the rates of atrazine dissipation between soils that were autoclaved and those that were not, especially for acidic soils. In alkaline soils, atrazine dissipation was somewhat faster in the natural soils, showing that microbial metabolism had an influence on atrazine fate. Therefore, concentrations of applied atrazine are not static in soils, but will tend to decline over time. It appears that for neutral to acidic soils, these dissipation processes can be primarily abiotic.

6.4.4 Other Environmental Media

Atrazine has been detected in oceans, at concentrations ranging from 1 to 100 ng/L and in estuaries at concentrations of 200 ng/L (Bester and Huhnerfuss 1993). Concentrations were generally higher closer to shore, and the monitoring study demonstrated that the Elbe River estuary, located in Germany, is highly contaminated with atrazine.

In fish, atrazine had a bioconcentration factor (BCF) of <10 in *Leuciscus idus* (golden orfe), after a 3-day exposure. In *Cyprinus carpio* (common carp), the measured BCF was 3–4 in some tissues (liver, kidney, and intestine) but only 1 for blood, muscle, and gills (Gluth et al. 1985). This suggests that atrazine does not bioaccumulate to a high degree in fish (Gluth et al. 1985). It has not been shown to bioaccumulate nor to be toxic to *Daphia magna*, at 10 µg/L (Baun and Nyholm 1996). BCF values measured for

D. magna in natural water were low, ranging from 2.4 to 3.0 (Akkanen et al. 2001). No toxic effects of atrazine were observed in *D. magna*, fathead minnows (*Pimephales promelas*), or tadpoles (*Rana pipiens*) in wetland mesocosms, at atrazine concentrations up to of 25 µg/L (for daphnia and tadpoles) or 75 µg/L (minnows) (Detenback et al. 1996).

6.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

According to the United States National Occupational Exposure Survey performed between 1981 and 1983 (NIOSH 1989), approximately 1,000 chemical industry workers, 123 of which were female, were potentially exposed to atrazine. Occupational exposure may occur through dermal exposure or inhalation exposure during the manufacture, formulation, and application of atrazine.

A study in Maryland examined pesticide metabolite concentrations in 80 randomly selected individuals from five counties. Exposure was evaluated by analysis of urine samples, and for atrazine, the presence of atrazine mercapturate (the primary excretory metabolite of atrazine) was evaluated. This metabolite was detected in only one sample out of the 348 total samples collected. In a similar study, 0.19% of 529 adults from the National Human Exposure Assessment Survey tested positive for atrazine mercapturate in urine samples (Needham et al. 2000).

FDA's Total Diet Study (TDS) has provided data on dietary intake of food contaminants for almost 40 years (FDA 2000b). It was initiated in 1961 as a program to monitor radioactive contamination in foods following atmospheric nuclear testing. Since then, it has been enlarged in scope to also monitor pesticides, industrial chemicals, toxic and nutritional elements, and vitamin residues in food. The analyses have been performed on foods that have been prepared for consumption, making the final results most relevant for a realistic estimate of dietary intake.

Even though atrazine is a widely used pesticide for corn and sugarcane, no atrazine residues were found in 16,648 samples of foods tested between 1991 and 1992 (IARC 1999) where a reporting limit of 50 µg/kg was used. Atrazine was found in residues of an unspecified number of foods in FDA analyses in only two of the years from 1993 to 1999 (FDA 1993, 1994, 1995b, 1996, 1997, 1998, 1999). In these analyses, atrazine was found in an unspecified number of foods in 1997 and 1999, but not in 1993, 1994, 1995b, 1996, or 1998. A recent FDA Total Diet Study (FDA 2000a) reported atrazine only in a roasted chicken sample at a concentration of 1 µg/kg. Similarly, the 1998 USDA Pesticide Data Program

reported that atrazine was not found in any of 6,643 fruit or vegetable samples, 585 milk samples, or 298 samples of corn syrup (USDA 1998). Limits of detection in these cases ranged from 0.01 µg/g or 0.01–0.33 µg/mL. In 1999, the same report noted that out of 6,419 fruit and vegetable measurements, atrazine was only detected once in a frozen spinach sample at a concentration of 0.028 µg/g. However, it was not detected in 156 analyses of corn syrup, where the limit of detection was 0.002 µg/mL (USDA 1999). These data suggest that most members of the general population have little or no exposure to atrazine from foods. In a study conducted in Germany, no atrazine was detected in several foods above allowable limits, when analyzed by a dipstick immunoassay approach (Wittmann et al. 1996). In these assays, allowable atrazine concentration limits were 10 mg/kg for mushrooms, spices, coffee, and tea; 1 mg/kg for sweet corn; 0.5 mg/kg for corn; and 100 µg/kg for other foods (Wittmann et al. 1996). In all samples analyzed, concentrations were below the detection limit of 0.3 µg/L, except for black aromatized tea, which had an atrazine concentration of 0.9 µg/L.

Drinking water analysis of agroecosystems in Ontario, Canada, for the years 1987–1991 showed atrazine concentrations ranging from 0.05 to 0.65 µg/L, with an average water concentration of 0.162 µg/L and a median concentration of 0.126 µg/L (Van Leeuwen et al. 1999).

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).

Even though children are exposed to a wide variety of chemicals, including atrazine, there is a lack of information from which to estimate their exposure (Quackenboss et al. 2000) to pesticides. It is expected,

however, that since children, due to their behavior and lifestyle, will be exposed to atrazine as a result of food preparation and their types of activities. Babies that are fed formula may be exposed to atrazine in drinking water due to their formula being reconstituted with drinking water collected from contaminated wells, as well as in their normal drinking water consumption. In addition, children may be exposed to atrazine from home and outside play activities. These would be as a result of playing on indoor floors that may have atrazine-containing dusts, or in yards or play areas outside that may contain atrazine.

A multipathway exposure assessment evaluated exposure of pesticides to children 3–12 years of age in the Minnesota Children's Pesticide Exposure Study (MNCPES), which was a project designed to acquire exposure information for children for a variety of pesticides, including atrazine (Quackenboss et al. 2000). This assessment sought to address multipath exposures from air, water, food, soil, and residential surfaces in the homes of the children. The study was designed to assess a wide range of households, so that different types of living conditions (rural vs. suburban households) could be compared and evaluated. A summary of the design strategy and implementation success (Quackenboss et al. 2000) reported that all samples had been collected and have been chemically analyzed, and the data were undergoing initial statistical analyses. Initial results from that study (Lioy et al. 2000) have shown that most atrazine is transported into the home by an unquantified and unidentified transport mechanism, thought to be tracking of soil into the home on shoes and feet (Lioy et al. 2000). Analysis of the home environment showed that it was present in 62 of 102 surface samples of the homes, in 61 of 102 carpet samples, and in 12 of 100 children hand rinse samples, but only in 2 of 89 of the urine samples collected from the children in the study. Ranges of atrazine in the homes ranged from 0.04 to 6.5 μg/mL of the samples collected from the surfaces (expressed in terms of uniform amounts of solution used to extract the sampling material). The relatively common occurrence of atrazine (in more than half of the environmental samples) show that children may be exposed to atrazine. Initial analysis of the urine samples, however, showed rare occurrence within potentially exposed children, as only 2 of 89 children had detectable levels of atrazine in the urine with concentrations ranging from 0.6 to 22 μg/g creatine (Lioy et al. 2000).

However, recent reports have suggested that more data are needed. According to a Federal Insecticide Fungicide and Rodenticide Act (FIFRA) report on the hazard and dose-response assessment of atrazine (Dorsey and Portier 2000), there are not enough data on the risk of atrazine to children, because exposure data are not available.

6.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Populations with potentially high exposures include pesticide, manufacturing, and railway workers. Data, however, exist mainly for pesticide workers (IARC 1999). Denovan et al. (2000) studied the levels of atrazine exposure in herbicide appliers by monitoring concentrations in saliva. Fifteen male pesticide appliers were invited to take part in the analysis through NIOSH screening procedures. Saliva concentrations of atrazine were significantly higher on the days that the herbicide was applied, in comparison to the days when it was not applied. Salivary concentrations were shown to peak in the afternoon (between 4 and 6 pm) of the day that the atrazine was sprayed, but concentrations decreased by bedtime, and were further reduced by the next morning. Based on observed deviations between subjects, saliva concentrations of >10 μg/L were determined to be a plausible predictor of an atrazine exposure. While concentrations of atrazine were higher in the samples collected at the end of the work day, atrazine concentrations in the saliva the morning following application were not statistically different from concentrations on nonspray days, but were approximately twice that of the preseason atrazine saliva concentrations. The median preseason concentration of 0.9 μg/L saliva may represent normal background exposure concentrations, since these samples were collected 1 month before the spraying season, or they could represent elimination of fat-stored atrazine. Alternatively, they could indicate low-level exposure to atrazine during work near atrazine-contaminated surfaces at the workplace (Denovan et al. 2000).

Other studies conducted on Italian herbicide workers (Catenacci et al. 1990) and on Finnish railway workers (Ikonen et al. 1988) demonstrated that urinary atrazine concentrations correlated with atrazine concentrations in the air during the work shift, and that the highest amounts of atrazine or atrazine metabolites in the urine were excreted either during or immediately following the exposure. A second study of Italian herbicide workers, however, showed no correlation between ambient air concentrations and urinary excretion concentrations (Catenacci et al. 1993). Differences were determined to be related to the differential dermal exposure of some workers to atrazine. Worker exposure was estimated to range from $4x10^{-6}$ mg/kg/hour for an enclosed cab ground applicator applying atrazine to sorghum, up to a high of $1.6x10^{-3}$ mg/kg/hour for mixer/loader applicators working on open cab applicators on Florida sugar cane (IARC 1999; Lunchick and Selman 1998).

As noted in Section 6.4.2, based on a 5-year NPS, the EPA estimated that atrazine was present in 1,570 CWS wells nationwide (EPA 1990a). Due to the statistical nature of the estimation calculation used, the estimates range from a low of 420 to a high of 2,701 CWS wells. The EPA also estimated that there are 70,800 rural domestic wells contaminated with atrazine (estimates range from a low of 13,300 to

a high of 214,000) (EPA 1990a). The estimates assume only that the concentration of atrazine would be above the limits of detection (0.12 µg/L) used in the survey. However, the maximum atrazine concentration detected in a CWS well was 0.92 µg/L; the maximum concentration detected in a rural domestic well was 7.0 µg/L (EPA 1990a). A more recent report found maximum seasonal and annual average concentrations of atrazine plus chlorinated metabolites to be 61.6 and 18.9 ppb, respectively, during a 1993–1998 monitoring program of 13 CWS in the United States that use surface water (EPA 2002b). It is noted that atrazine is generally found at higher concentrations in CWS that use surface water sources compared to those that use groundwater sources.

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 atrazine 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 atrazine.

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 atrazine are sufficiently well defined to allow assessments of the environmental fate of atrazine to be made (Bailey et al. 1968; Brown and Flagg 1981; Dousset et al. 1994; Green et al. 1993; Hansch et al. 1995; HSDB 2002; Humburg 1999; IARC 1999; Koskinen and Rochette 1996; Meakins et al. 1995; Reiderer 1990; Tomlin 1997; Verschueren 2001; Ward and Weber 1968; Weber 1991), and no additional information is needed.

Production, Import/Export, Use, Release, and Disposal. Information is needed that provides more recent estimates or actual values for quantities of atrazine that are produced, imported, and exported, as well as more data on the amounts used in agriculture and other weed-control applications.

Environmental Fate. The fate of atrazine has been well-studied and reviewed in the current literature. Due to its widespread usage, it is one of the best studied pesticides (IARC 1999; Koskinen and Clay 1997); however, biodegradation has rarely been documented in soils or in groundwater, suggesting that indigenous microorganisms that degrade atrazine are lacking. Since atrazine is observed to undergo degradation in some soils, more environmental fate studies are needed to determine the factors and mechanisms that permit degradation in these soils compared to soils where it is not observed. In addition, to better understand how atrazine interacts with the soil environment, more research is needed to determine the nature of the sorptive interaction(s) between atrazine and the particulate and chemical environment of different soils. This will provide either an explanation of the relatively wide range of observed K_{oc} values, or it may provide a better estimate of its true K_{oc}.

Bioavailability from Environmental Media. No additional information on the bioavailability of atrazine from environmental media is warranted at this time.

Food Chain Bioaccumulation. Little food chain accumulation of atrazine has been observed, as it does not tend to bioaccumulated; thus, no additional data are needed.

Exposure Levels in Environmental Media. No additional information on exposure levels of atrazine in environmental media is warranted at this time.

Exposure Levels in Humans. Due to the widespread usage of atrazine, but lack of toxicological effects, more data are needed to verify whether exposures to atrazine can lead to toxicological effects. Most exposure level evaluations have occurred in applicators; more data are needed for farmers.

Exposures of Children. There is current research evaluating pesticide exposures to children in Minnesota. However, more data are needed, as is indicated in the FIFRA report on the hazard and dose-response assessment of atrazine (Dorsey and Portier 2000). This research should yield valuable information regarding childhood atrazine exposures in the near future.

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 atrazine were located. This substance 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 the 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 this substance.

6.8.2 Ongoing Studies

The Federal Research in Progress (FEDRIP 2002) database and the Current Research Information System (CRIS 2002) provide additional information obtainable from ongoing studies that may fill in some of the data needs identified in Section 6.8.1. These studies are summarized in Table 6-2. The successful completion of these projects will contribute to better understanding of environmental fate of atrazine, a better set of approaches to study the fate of atrazine in environmental matrices, and a better set of agricultural practices that could reduce the levels of atrazine exposure to humans.

Research planned by the EPA will involve monitoring of triazines and their degradation products (including atrazine) in drinking water as prescribed by the Safe Drinking Water Act (SDWA) for chemicals on the Contaminant Candidate List (CCL). EPA will use these data to determine if further regulation is required for these chemicals according to the SDWA.

Table 6-2. Ongoing Studies on the Potential for Human Exposure to Atrazine

Investigator	Affiliation	Research description	Sponsor
Bleam W	University of Wisconsin, Madison, Wisconsin	Analysis of hydrogen bonding of atrazine by NMR approaches. Goal is to better describe interactions of atrazine with soil organic matter.	National Center for Research Resources
Camper ND, Riley MB	Clemson University, Clemson, South Carolina	Evaluation of SPE approaches for improving extraction of and stabilization of pesticides from water samples. Sampling and approaches were tested, and stability of environmental samples was shown to be better when shipped in SPE matrices as compare to shipment of water samples. Should lead to better accuracy of determinations of pesticides in aquatic matrices.	Hatch award
Currie RS	CSREES, Kansas	Evaluation of registered and experimental herbicides in replicated experiments for weed control and crop tolerance. Weed control tactics will be developed that integrate cultural, mechanical, and chemical weed control methods. Biological, physiological, and ecological characteristics of some major weed species and the interactive affects in crops will be studied.	Hatch
Grichar WJ	Texas A&M University, College Station, Texas	Develop cultural practices that increase soil stability, reduce wind and water erosion. Found that some combinations of atrazine with other pesticides (pendimethalin) resulted in stunted grain sorghum growth.	Hatch
Griffin JL	Lousiana State University, Baton Rouge, Louisiana	Determine efficacy of pre- and post-emergence herbicides on common weeds in southern Louisiana crops. Found that weeds common in sugar cane crops were not resistant to atrazine, but that the atrazine was not commonly applied at the correct time for control of this weed.	Hatch
Huang H-M	Jackson State University, Jackson, Mississippi	Examination of the relative and combined roles of photolysis and microbial degradation on the fate of atrazine in surface waters, as well as to assess mutagenicity or toxicity of reaction products.	National Institute of General Medical Sciences
Johnston CT	CSREES, Indiana	Development of improved models to predict pesticide fate and transport in soils based on soil sorption data.	Hatch
Leidy RB	North Carolina State University, Raleigh, North Carolina	Development of SPE approaches for collection and stabilization of pesticides from water samples. Research will try to demonstrate that the SPE disks improve stability of sample during transport (over shipment of water samples), and will result in less error between test labs.	Hatch
Leidy RB	North Carolina State University, Raleigh, North Carolina	Validate methods for analyses conducted with 3M Empore disc membranes for pesticides including atrazine.	Hatch

Table 6-2. Ongoing Studies on the Potential for Human Exposure to Atrazine

Investigator	Affiliation	Research description	Sponsor
Montvaldo R et al.	University of Puerto Rico, Mayaguez, Puerto Rico	Evaluation of SPE approaches for sampling water for pesticides. Testing of sample showed excellent recoveries of test pesticides. Will lead to better analysis of pesticides in field samples by minimizing transportation and storage losses.	Hatch
Mueller TC	University of Tennessee, Knoxville, Tennessee	Evaluation of SPE approaches for stabilization of pesticides in water. Research demonstrated that the SPE approaches improved pesticide stability during transport.	Hatch
Nkedi-Kizza P	SAES, Florida	Examination of the influence of physical, chemical, and mineralogical soil properties that influence the fate and transport of organic pesticides in the environment.	State
Pignatello JJ, Xing B	CSREES, Connecticut	Investigation of the causes of “non-ideal” sorption and development of experiments to further test a previous hypothesis that soil organic matter behaves like a glassy polymer in regard to its sorptive properties.	Cooperative agreement
Radosevich M et al.	CSREES, Delaware	Investigation of the link between the diversity, frequency, and expression of genes encoding the atrazine degradative pathway and observed aerobic and anaerobic degradation rates in environments with and without a prior history of atrazine application.	NRI
Senseman SA	Texas A&M University, College Station, Texas	Investigation of the environmental fate of herbicides in water, soil, and plants by evaluation of runoff, sorption, and degradation of herbicides in different environmental compartments. Examined SPE extraction, along with supercritical fluid extraction from samples.	Hatch
Sims GK, Wax LM	Agricultural Research Service, Illinois	Identification of mechanisms of herbicide persistence associated with carryover damage and offsite movement. Study of the susceptibility of weed seeds to microorganisms during seed decay, the role of microbial inhibition in biodegradation of herbicides with anti-microbial properties. Exploration of practical approaches to enhance degradation of xenobiotics used in agricultural production.	USDA
Spalding RF	CSREES, Nebraska	Examination of the impact of management alternatives on groundwater and surface water quality and development of *in situ* aquifer methods to remediate groundwater nitrate concentrations.	Hatch
Yoder RE et al.	University of Tennessee, Knoxville, Tennessee	Investigation of agricultural production systems that minimize off-site movement of pesticides. Monitored surface flow, developed better surface maps, and analyzed these to better predict surface solute transport. Monitored atrazine surface and soil transport.	Hatch

Table 6-2. Ongoing Studies on the Potential for Human Exposure to Atrazine

Investigator	Affiliation	Research description	Sponsor
Zhu KY	CSREES, Kansas	Elucidation of chemical and biochemical mechanisms and pathways of pesticide residue degradation including characterization of degradation products. Characterization and quantification of exposure and effects of pesticides and their degradation products on target and nontarget organisms.	Hatch

[a]Source: CRIS 2002; FEDRIP 2002

CSREES = Cooperative State Research, Education, and Extension Service; NMR = Nuclear Magnetic Resonance; NRI = National Research Institute; SPE = solid phase extraction; USDA = U.S. Department of Agriculture