

5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Humans may be exposed to acrylonitrile through air, water and food. Acrylonitrile has been identified in 3 of 1,177 NPL sites. The frequency of these sites within the United States can be seen in Figure 5-1.

Acrylonitrile is readily volatile, and significant quantities escape into air during manufacture and use. Volatilization may also occur from hazardous waste sites. In air, acrylonitrile is degraded primarily by reaction with hydroxyl radicals, with an estimated half-life of 5 to 50 hours. Acrylonitrile has been detected in air in the vicinity of various industrial sources at concentrations from 0.1 to 325 ppb, but has not been detected in typical ambient air.

Acrylonitrile is also readily soluble in water, and current total discharges to water via industrial effluents are low. Water contamination may also occur following a spill or near a chemical site. In water, acrylonitrile has little tendency to adsorb to sediment, but is subject to biodegradation by microorganisms. The rate and extent of degradation depend upon conditions and upon the time for Microbiol acclimation. Degradation may approach 100% under favorable circumstances, but may be inhibited by high concentrations of acrylonitrile.

For members of the general public who do not live near an industrial source or a chemical waste site, exposure to very low levels of acrylonitrile may occur through contact with consumer products such as acrylic carpeting or by ingestion of food stored in acrylic plastic containers. Acrylonitrile may enter human food materials by leaching from plastic food containers. For people who do live near such a source, inhalation of acrylonitrile in air is likely to be the main route of exposure, although intake through water could also be of concern. Inhalation of acrylonitrile in air may be much higher for workers in industries that produce or use acrylonitrile. Acrylonitrile has been detected in surface water and groundwater near some industrial sources and hazardous waste sites, usually at concentrations between 20 and 4,700 ppb.

5.2 RELEASES TO THE ENVIRONMENT

5.2.1 Air

Because acrylonitrile is readily volatile, significant releases to air may occur during acrylonitrile production and use (Hughes and Horn 1977; Miller and Villaume 1978). Kayser et al. (1982) estimated that 11,790 kkg/yr (metric tons per year) of acrylonitrile was released from these sources, accounting for 87% of all acrylonitrile released to the

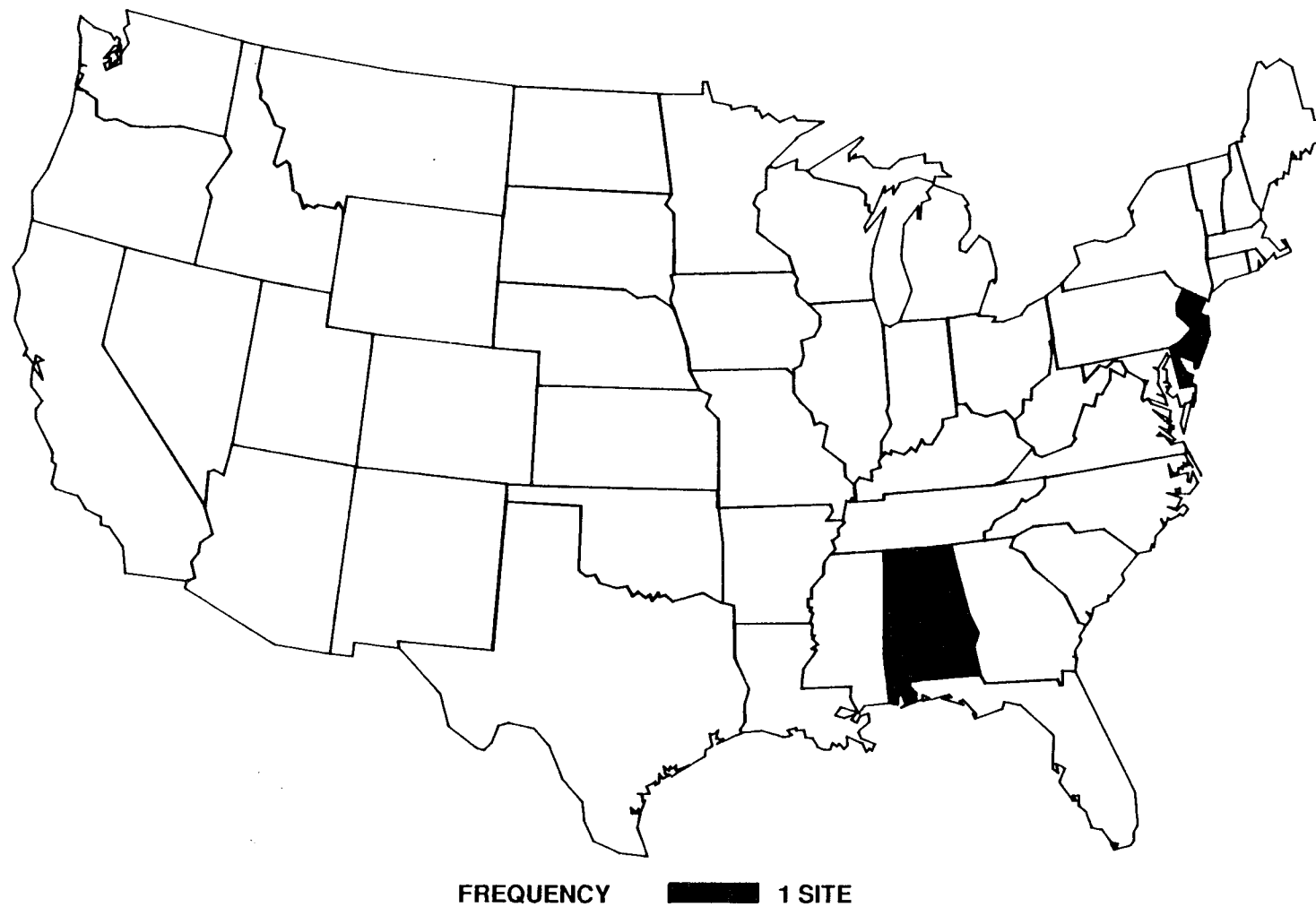


FIGURE 5-1. FREQUENCY OF SITES WITH ACRYLONITRILE CONTAMINATION

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environment. Quantitative data on air releases from other sources were not located, but volatilization might be significant following a spill or in the vicinity of a chemical waste site containing acrylonitrile.

5.2.2 Water

Acrylonitrile may also be released to water during production and use. According to data collected under SARA 313, total reported releases to water during 1987 were 0.9 metric tons (TRI 1988). No data were located on acrylonitrile releases to water from other sources, but because acrylonitrile is readily soluble and is not strongly adsorbed to soil or sediment (see Section 5.3.1 below), large accidental spills or leaks from chemical waste sites could lead to significant water contamination. While acrylonitrile is rapidly biodegraded in water, high concentrations may inhibit degradation. Several examples of groundwater contamination following spills have been reported (Miller and Villaume 1978). Acrylonitrile may also be released to water by leaks or emissions from hazardous waste sites. Acrylonitrile has been detected in surface water at 2 sites and in groundwater at 5 sites of 862 hazardous waste sites (including NPL and other sites) being investigated under Superfund (CLPSD 1988).

5.2.3 Soil

Direct release of acrylonitrile to soil during acrylonitrile production and use is believed to be minimal (less than 1 kkg/yr) (Kayser et al. 1982). Accidental spills or leaks from hazardous waste sites could lead to local areas of soil contamination, and acrylonitrile has been detected in soil at 3 chemical waste sites (NPL and other sites) being investigated under Superfund (CLPSD 1988).

5.3 ENVIRONMENTAL FATE

5.3.1 Transport and Partitioning

Acrylonitrile is both readily volatile in air (0.13 atm at 23°C) (Mabey et al. 1982) and highly soluble in water (79,000 mg/L) (Klein et al. 1957). These characteristics dominate the behavior of acrylonitrile in the environment. While present in air, acrylonitrile has little tendency to adsorb to particulate matter (Cupitt 1980), so air transport of volatilized material is determined mainly by wind speed and direction. Similarly, acrylonitrile dissolved in water has only a low tendency to adsorb to suspended soils or sediments (Roy and Griffin 1985), so surface transport is determined by water flow parameters. Based on its relatively high water solubility, acrylonitrile is expected to be highly mobile in moist soils. In addition, acrylonitrile may

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penetrate into groundwater from surface spills or from contaminated surface water. The high vapor pressure indicates that evaporation from dry soil samples is expected to occur rapidly (EPA 1987).

The tendency of acrylonitrile to partition between air and water is described by Henry's law constant (H). The value of H for acrylonitrile has not been determined experimentally, but has been calculated to be 8.8×10^{-5} atm-m³/mole (Mabey et al. 1982). This value indicates that acrylonitrile will occur in both air and water, tending to transfer between air and water phases only slowly. Cupitt (1980) estimated the half-time of acrylonitrile clearance from air in wet precipitation to be greater than 10 months.

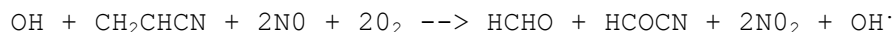
Based on the relatively low value of the octanol/water partition coefficient (K_{ow}) for acrylonitrile ($\log K_{ow} = -0.92$) (Verschueren 1983), it would not be expected that acrylonitrile will strongly bioaccumulate in the tissues of aquatic organisms (Kenaga 1980; Neely et al. 1974). However, data in aquatic organisms exposed to water containing acrylonitrile show that it does accumulate in fat tissue. Barrows et al. (1978) measured a steady-state bioconcentration factor (BCF) of 48 in bluegill sunfish. Based on the relative proportion of fat in sunfish and other aquatic organisms, EPA (1980a) estimated an average BCF of about 30 for the edible portions of freshwater and marine species.

5.3.2 Transformation and Degradation

5.3.2.1 Air

The principal pathway leading to degradation of acrylonitrile in air is believed to be photooxidation, mainly by reaction with hydroxyl radicals (OH). The rate constant for acrylonitrile reaction with OH has been measured as 4.1×10^{-12} cm³/molecule/second (Harris et al. 1981). This would correspond to an atmospheric half-life of about 5 to 50 hours. This is consistent with a value of 9 to 10 hours measured in a smog chamber (Suta 1979).

The photooxidation of acrylonitrile by hydroxyl radicals in the presence of nitric oxide has been observed to yield formaldehyde (HCHO) and formyl cyanide (HCOCN) (Hashimoto et al. 1984). From these results, the following reaction was proposed:



Data given by Hashimoto et al. (1984) suggest that the half-life of acrylonitrile in the atmosphere may be on the order of 12 hours.

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Acrylonitrile may also be oxidized by other atmospheric components such as ozone and oxygen, but the rates of these reactions are much lower than for OH. and are not considered to be an important degradative pathway (Harris et al. 1981).

5.3.2.2 Water

Very little is known about nonbiologically mediated transformations of acrylonitrile in water. There are no data to suggest that acrylonitrile hydrolyzes under ambient conditions. While it is known that acrylonitrile photooxidizes in air, no reliable information was found on photochemical reactions in water. There were also no data on the oxidation of acrylonitrile in water. Acrylonitrile is susceptible to oxidation by strong oxidants such as chlorine used to disinfect drinking water.

Acrylonitrile is readily degraded by aerobic microorganisms in water, especially if there is time for acclimation (Cherry et al. 1956; Mills and Stack 1953, 1955; Stover and Kincannon 1983). After 27 days of acclimation, about 70% of the acrylonitrile initially present in river water was degraded under laboratory conditions, yielding acrylic acid and ammonia. Complete degradation occurred under ideal conditions where nutrients were added to promote Microbiol growth (Cherry et al. 1956).

A bacterium classified as Nocardia rhodochrous LL 100-2 has been reported to be able to degrade acrylonitrile (DiGerónimo and Antoine 1976). An aerobic bacterium classified as Arthrobacter in an acclimated sludge depletely degraded acrylonitrile after 48 hours yielding acrylic acid (Yamada et al. 1979). It was proposed that acrylonitrile was biodegraded by the following reaction:



It has been shown that low concentrations of acrylonitrile in solution (10 mg/L or less) can be completely degraded in a laboratory, static-culture batch experiment where domestic sewage water was the source of the Microbiol inoculum (Tabak et al. 1981). A solution of acrylonitrile (152 mg/L) was degraded to less than 0.05 mg/L in a continuous flow activated sludge system under laboratory conditions (Kincannon et al. 1983).

Studies performed using sewage sludge indicate that acrylonitrile may also be degraded by methanogenic bacteria under anaerobic conditions, although concentrations of 50 to 1,000 mg/L lead to moderate inhibition of bacterial fermentation (Miller and Villaume 1978). This

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suggests that Microbiol degradation of acrylonitrile in anaerobic groundwater may not proceed efficiently if acrylonitrile levels were high, as might occur after a spill.

5.3.2.3 Soil

No studies were located regarding the biodegradation of acrylonitrile in soil. However, it seems likely that acrylonitrile in moist soil would be subject to biodegradation similar to that observed in aerobic water, although degradation rates might differ.

5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT

5.4.1 Air

Acrylonitrile has not been found to occur at measurable concentrations in ambient air (Brodzinsky and Singh 1983). Measurable levels of atmospheric acrylonitrile are associated with industrial sources.

Air samples collected in one acrylonitrile-fiber plant ranged from 3 to 20 mg/m³ (EPA 1980a). Mean 24-hour acrylonitrile concentrations in atmospheric samples collected within 5 km of 11 factories producing or using acrylonitrile ranged from less than 0.1 to 325 µg/m³ (Suta 1979). The occurrence of acrylonitrile was correlated to wind patterns; the highest concentrations were downwind of and in close proximity to the plant. The median concentration of acrylonitrile for 43 measurements in "source-dominated areas" (i.e., near chemical plants) was 2.1 µg/m³ (Brodzinsky and Singh 1983). There were no data available on the concentration of acrylonitrile in air near chemical waste sites, but because acrylonitrile is easily volatilized, this is an exposure pathway of concern.

5.4.2 Water

Acrylonitrile is not a common contaminant of typical surface water or groundwater. In a state-wide survey of over 1,700 wells in Wisconsin, acrylonitrile was not detected in any sample (Krill and Sonzogni 1986). Acrylonitrile was detected in 46 of 914 samples of surface water and groundwater taken across the United States (Staples et al. 1985), generally at levels less than 10 ppb.

The most likely source of acrylonitrile in water is industrial discharges. Levels of acrylonitrile measured in the effluents from a variety of industrial sites (iron and steel factories, textile mills, chemical plants) have ranged from 20 to 4,700 ppb, resulting in

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concentrations in nearby rivers ranging from below detection limits to 4,300 ppb (EPA 1983c). Data collected under SARA indicated total discharges to water during 1987 were 0.9 metric tons (TRI 1988).

Another source of acrylonitrile in water is leachate from chemical waste sites. Preliminary data from the Contract Laboratory Program (CLP) Statistical Database indicates that acrylonitrile has been detected in surface water samples collected at two of 862 hazardous-waste sites (including NPL and other sites) being investigated under Superfund. The median concentration of the positive samples was 100 µg/L (CLPSD 1988). Acrylonitrile was detected in 12 groundwater samples collected at 5 sites, also at a median concentration of 100 µg/L.

5.4.3 Soil

Staples et al. (1985) reported that acrylonitrile was not present at detectable concentrations in 351 sediment samples collected from lake and river bottoms across the United States. Preliminary data from the Contract Laboratory Program (CLP) Statistical Database (CLPSD 1988) indicated that acrylonitrile was detected in soils at 3 of 862 hazardous waste sites (including NPL and other sites) being investigated under Superfund. The median concentration of five samples was 120 µg/kg.

5.4.4 Other Media

Foods may become contaminated with acrylonitrile as a result of the migration of the monomer from chemical containers made of acrylonitrile polymers. Acrylonitrile has been found to desorb from polyacrylonitrile resins and partition into cooking oil (Gilbert et al. 1980). Other foods which may be contaminated by acrylonitrile from their containers include luncheon meat, peanut butter, margarine, fruit juice, and vegetable oil (EPA 1980a, 1983c; FDA 1984). There are few data on the extent of food-related acrylonitrile exposure. The FDA reported typical acrylonitrile concentrations in margarine of 25 µg/kg (FDA 1984), and the Commission of European Communities (1983) reported that the levels of acrylonitrile in contaminated foods are generally about 1 µg/kg. While past data suggest potential exposure, there is little current migration of the monomer from current packaging materials because food is packaged in vastly different resins that have been drastically improved (AN Group 1990).

Acrylonitrile was detected in the smoke of cigarettes made in the United States in the 1960s and 1970s, usually at levels of 1 to 2 mg per cigarette (IARC 1979). At that time, acrylonitrile was used as a fumigant for stored tobacco. Most pesticide registrations for acrylonitrile were cancelled in 1978, and the use of acrylonitrile as a

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fumigant has been discontinued. Although no data were located, cigarette smoking is probably no longer a major source of human exposure to acrylonitrile.

Residual acrylonitrile monomer may also occur in commercially-made polymeric materials used in rugs and other products. Estimated levels include acrylic and modacrylic fibers (less than 1 mg acrylonitrile/kg polymeric material), acrylonitrile-based resins (15 to 50 mg/kg), and nitrile rubber and latex (0 to 750 mg/kg) (IARC 1979; Miller and Villaume 1978). It is possible that acrylonitrile may evaporate into air or leach into water from these products, but no data on this topic were located.

5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE

As shown in Table 5-1, only people living near chemical factories or work sites are likely to be exposed to measurable amounts of acrylonitrile in air and water. Dispersion modeling studies have indicated that approximately 2.6 million people living within 30 km of emission sources may be exposed to atmospheric acrylonitrile (Suta 1979). Members of the general population may also be potentially exposed to acrylonitrile through the consumption of acrylonitrile-contaminated food. However, it should be recalled that only foods in direct contact with acrylonitrile-based plastics are subject to contamination, and then only at very low levels.

Occupational exposures via inhalation of acrylonitrile vapor at the work place are likely to be considerably greater than exposures outside the workplace (Table 5-1). Exposure levels may be highest for workers in plants where the chemical is synthesized (EPA 1984).

5.6 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

It has been estimated that over 100,000 workers are potentially exposed to acrylonitrile during production and use (NIOSH 1977, 1988). Occupational exposures include plastic and polymer manufacturers, polymer molders, polymer combustion workers, furniture makers, and manufacturers of fibers and synthetic rubber (EPA 1980a). Other populations who could have elevated exposure to acrylonitrile are residents in the vicinity of industrial sources or chemical waste sites.

5.7 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, 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 acrylonitrile is available. Where adequate information is not available, ATSDR, in conjunction with the NTP, is

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TABLE 5-1. Estimated Levels of Human Exposure to Acrylonitrile for Nonoccupational and Occupational Exposure

Population Type	Medium	Typical Concentration in Medium	Assumed Rate of Intake of Medium	Assumed Absorption Fraction	Estimated Dose ($\mu\text{g}/\text{kg}/\text{day}$)
General ^a (70-kg Adult)	Air	0.0 $\mu\text{g}/\text{m}^3$	20 m^3/day	0.9	0
	Water	0.0 $\mu\text{g}/\text{L}$	2 L/day	0.9	0
	Food	1 $\mu\text{g}/\text{kg}$	2 kg/day	0.5	0.01
Population living within 5 km of a chemical factory or waste site	Air	2 to 12 $\mu\text{g}/\text{m}^3$	20 m^3/day	0.9	0.5 to 3.0
	Water ^b	0.1 $\mu\text{g}/\text{L}$	2 L/day	0.9	0.003
Workers in an acrylonitrile factory	Air	0.1 to 4 mg/m^3	10 m^3/day	0.9	12.9 to 514

^aPotential exposures from chemical spills and acrylic clothing were not considered.

^bUntreated well water assuming waste effluent or leachate initially containing 10 $\mu\text{g}/\text{L}$ is reduced by a factor of 100 by groundwater dilution and biodegradation before it reaches the well.

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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 acrylonitrile.

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 or eliminate the uncertainties of human health assessment. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

5.7.1 Identification of Data Needs

Physical and Chemical Properties. Most of the important physical-chemical properties of acrylonitrile have been determined (see Chapter 3). However, the partitioning of acrylonitrile between the air and water has been evaluated by using an estimated value for a Henry's law constant. This general approach assumes that the concentration of the chemical in water is low. Because acrylonitrile is relatively soluble in water, this approach may not be accurate. Experimental measurement of the partition coefficient for acrylonitrile at water-air interfaces would be useful in refining models on the behavior of acrylonitrile in the environment.

Production, Use, Release and Disposal. Substantial data exist on past production, use and emissions of acrylonitrile in the United States. Data on current releases to the environment and disposal practices are collected under SARA 313. Additional studies are not needed at this time because these data are readily available.

According to the Emergency Planning and Community Right to Know Act of 1986 (EPCRTKA), (§313), (Pub. L. 99-499, Title III, (§313), industries are required to submit release information to the EPA. The Toxic Release Inventory (TRI), which contains release information for 1987 and 1988, became available in May of 1989. This database will be updated yearly and should provide a more reliable estimate of industrial production and emission.

Environmental Fate. Laboratory studies indicate that acrylonitrile is biodegraded in aqueous systems promoting microbial growth, but typical degradation rates in lakes or rivers have not been studied in detail. Similarly, it is not known if acrylonitrile will biodegrade significantly in soil. Data on the chemical oxidation, photodegradation, and biodegradation of acrylonitrile in surface and groundwater would be helpful.

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Bioavailability from Environmental Media. There are limited data on the bioavailability of acrylonitrile in different environmental media. Data on the bioavailability of acrylonitrile would be valuable.

Food Chain Bioaccumulation. There are no data on the bioaccumulation of acrylonitrile in the food chain. The lack of data may not be a major limitation, because limited data suggest that acrylonitrile has a relatively low tendency to be bioconcentrated by lower trophic levels.

Exposure Levels in Environmental Media. Existing studies have not provided data on acrylonitrile levels in typical ambient air. Studies using analytical methods with lower detection limits would be helpful in determining if ambient air is an exposure medium of concern. Because higher levels of exposure are most likely near industrial sources or chemical waste sites, additional data on the occurrence of acrylonitrile in the atmosphere, surface water, and groundwater near such sites would be useful.

Exposure Levels in Humans. Human exposure levels to acrylonitrile can only be estimated based on average concentrations in air, food and water. Direct studies of personal exposure levels for individuals with exposures judged to be average and above average (e.g., people living near industrial sources or hazardous waste sites) would be helpful in improving total dose estimates, and in identifying exposure pathways of concern.

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

5.7.2 On-going Studies

The Acrylonitrile Group, Inc. is currently performing an acrylonitrile degradation study in groundwater and surrounding soil to obtain kinetic data for hydrolysis, biodegradation, primary metabolites and rates of mineralization. Radiolabeled material at three concentrations over three orders of magnitude will be used. The data will also establish the effect of accumulation on biodegradation kinetics.