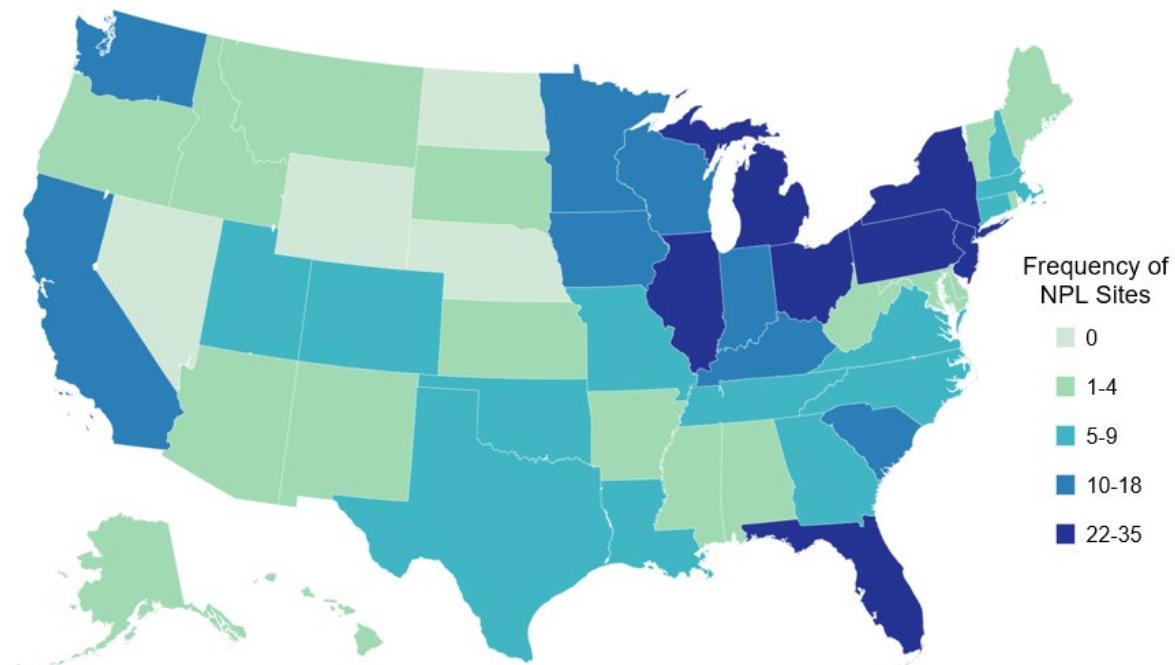


CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Cyanide (reported as cyanide, hydrogen cyanide, sodium cyanide, potassium cyanide, or copper (I) cyanide) has been identified in at least 459 of the 1,868 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2022a). However, the number of sites in which cyanide has been evaluated is not known. The number of sites in each state is shown in Figure 5-1.

Figure 5-1. Number of NPL Sites with Cyanide Contamination



Source: ATSDR 2022a

- The primary route of exposure for the general population to hydrogen cyanide is via inhalation of cigarette smoke and the consumption of certain foods.
- Occupational exposure may occur in facilities that use hydrogen cyanide.
- Since hydrogen cyanide has a very high vapor pressure and Henry's law constant, it is expected to volatize rapidly and exist primarily in the vapor phase.
- In the atmosphere, the main degradation pathway of hydrogen cyanide will be through its reaction with photochemically generated hydroxyl radicals.

5. POTENTIAL FOR HUMAN EXPOSURE

- Unless microorganisms are acclimated to hydrogen cyanide, biodegradation is not likely to play a large role at high concentrations due to the toxicity of cyanide compounds.

The descriptor cyanogenic in this Toxicological Profile refers to a compound that releases the cyanogen radical or the cyanide anion. Since the CN portion of the compound is of concern in poisons, any reference to the amount present in air, water, soil, sediments, or other media refers only to this part of the compound. The term free cyanide refers to hydrogen cyanide and cyanide anion (CN^-) (EPA 1981; Oudjehani et al. 2002; Shifrin et al. 1996; WHO 2004).

Anthropogenic (of human origin) sources are responsible for much of the cyanide in the environment. Cyanide-containing substances also occur naturally in the fruits, seeds, roots, and leaves of numerous plants, and are released to the environment from natural biogenic processes from higher plants, bacteria, and fungi (Cicerone and Zellner 1983; Crutzen and Carmichael 1993; EPA 1981; Jones 1998; Knowles 1988; Mudder and Botz 2000). Certain species of millipedes contain cyanogenic compounds (e.g., benzoyl cyanide) in their chemical defense glands that release hydrogen cyanide once secreted (Shear 2015). However, an estimate of the amount of cyanide released to the environment from natural biogenic processes is not available. The major cyanide releases to water are discharges from metal-finishing industries, iron and steel mills, and organic chemical industries (WHO 2009). Effluents from the cyanidation process used in precious metal extraction contain high amounts of cyanide (WHO 2009). The contribution of this source to the total cyanide discharge in water is insignificant on average (EPA 1981). However, large, short-term releases can occur from the failure of tailing ponds resulting in the introduction of high concentrations of cyanide into local surface waters and subsoils (Fields 2001; Mudder and Botz 2000). Vehicle exhaust (Baum et al. 2007) and biomass burning (Le Breton 2017) are major sources of cyanide released into the air. The major sources of simple and complex cyanide releases to soil appear to be from the disposal of cyanide wastes in landfills and the use of cyanide-containing road salts (Pandolfo et al. 2012; Jaszcak et al. 2017). Cyanogen chloride is formed in drinking water from reaction of humic substances with chloramine produced during chlorination (WHO 2009). Thiocyanate is released to water primarily from discharges of industrial wastewaters from coal processing and extraction of gold and silver (Boucabeille et al. 1994a); the thiocyanate is formed from the reaction of sulfur donors that are present in coal and crushed rock with the cyanide that is used in the processing of these materials. Thiocyanate is also found in mining wastewaters where it results from the interaction of the cyanide anion (CN^-) with sulphur (Boucabeille et al. 1994b). Releases of thiocyanate to soil result from anthropogenic and natural sources. Anthropogenic releases occur primarily from direct application in herbicidal formulations and from disposal as byproducts from industrial processes. Nonanthropogenic sources

5. POTENTIAL FOR HUMAN EXPOSURE

include damaged or decaying tissues of plants from the family *Brassica* (e.g., cabbage, mustard, kale) (Brown and Morra 1993).

Cyanide is released into air mainly as hydrogen cyanide gas and, to a lesser extent, as particulate cyanides. Hydrogen cyanide can potentially be transported over long distances before reacting with photochemically generated hydroxyl radicals. The residence time of hydrogen cyanide in the atmosphere has been estimated to be approximately 2.5 years, with a range of 1.3–5.0 years, depending on the hydroxyl radical concentration (Cicerone and Zellner 1983). Neither photolysis nor deposition by rainwater is expected to be a significant removal mechanism. Only 2% of the tropospheric hydrogen cyanide is expected to be transported to the stratosphere (Cicerone and Zellner 1983). In water, cyanide occurs most commonly as hydrogen cyanide. Hydrogen cyanide is expected to be removed from water primarily by volatilization. Cyanide may also be removed by aerobic or anaerobic biodegradation (Akcil and Mudder 2003; EPA 1979, 1994). At soil surfaces, volatilization of hydrogen cyanide is a significant loss mechanism for cyanides. In subsurface soil, cyanide at low concentrations would probably biodegrade under both aerobic and anaerobic conditions. In cases where cyanide levels are toxic to microorganisms (i.e., landfills, spills), the concentrations of water-soluble cyanides may be sufficiently high to leach into groundwater.

The environmental fate of thiocyanate has not been thoroughly investigated. Aerobic and anaerobic biodegradation are significant transformation processes for thiocyanates in water (Boucabeille et al. 1994a, 1994b; Shivaraman et al. 1985) and soil (Brown and Morra 1993). At near-ambient temperatures, sorption and volatilization are not significant partitioning processes for thiocyanate in soil (Brown and Morra 1993).

Despite the various ways cyanide is thought to be released into the environment, recent monitoring data are limited. Cyanide levels in outdoor air range from 0.33 to 0.76 ppbv, with the highest levels measured near a gold heap leach field (Jaszczak et al. 2017). Compiled water-quality data from 1981–2023 in the Water Quality Portal (WQP) from the U.S. Geological Survey (USGS), EPA, and over 400 state, federal, tribal, and local agencies indicate that cyanide is a relatively common water pollutant and was detected in 37% of samples (WQP 2024). Less than 1% had values that were >10 µg/L, with 91 drinking/potable water samples with values between 10 and 50 µg/L.

Available monitoring data on thiocyanate are also very limited. No information was found in the available literature on major routes of exposure among the general population or on estimates of

5. POTENTIAL FOR HUMAN EXPOSURE

exposure. Because thiocyanate is a major metabolite of cyanide in the body, exposure to cyanide is a source of thiocyanate exposure. Thiocyanate occurs naturally in many edible plants. Vegetables in the family *Brassica* contain high levels of thiocyanate compounds (based on total glucosinolate concentrations) with concentrations ranging up to 1,172 µmol/100 g fresh weight (Felker et al. 2016). No data were found in the available literature on thiocyanate concentrations in surface water, groundwater, or drinking water.

The available data indicate that the general population is exposed to cyanide primarily by ingestion of foods that contain substances that release cyanides when ingested and through smoking, and to a lesser extent, by consumption of contaminated drinking water and inhalation of contaminated air. Dermal absorption is not a significant exposure route for the general population. Among the general population, subpopulations with the most likely potential of exposure to cyanide at concentrations higher than background levels include active and passive tobacco smokers (EPA 1981; Mahernia et al. 2015) and individuals who are exposed to house fires or other types of building fires (Andrews et al. 1989; Bolstad-Johnson et al. 2000). Subpopulations with potential for exposure to cyanides or thiocyanates are residents who live near industrial sites releasing these compounds to the environment, residents who live near cyanide- or thiocyanate-containing hazardous waste sites, and people who consume foods high in cyanogenic glycosides. The amount of cyanide in emissions from commonly sold tobacco products has not decreased significantly; therefore, older data regarding exposure may still be relevant (Mahernia et al. 2015). Fetuses of smoking mothers or mothers exposed to high levels of environmental smoke may also be at risk of exposure to relatively high concentrations of cyanide and thiocyanate (Bottoms et al. 1982; EPA 1992; Hauth et al. 1984). For example, mean thiocyanate concentrations of 88.6 and 32.0 µg/L have been measured in fetal blood of mothers who smoked or were exposed to passive smoke, as compared to a mean thiocyanate concentration of 24.3 µg/L in unexposed mothers (Bottoms et al. 1982).

Occupational exposures to cyanide occur primarily through inhalation and, less frequently, through dermal absorption. Workers may be exposed to cyanides in various occupations, including electroplating, metallurgy, pesticide application, firefighting, steel manufacturing, gas works operations, and metal cleaning (EPA 1981; NRC 2002; WHO 2004). The manufacture of industrial inorganic chemicals may be a potential source of occupational exposure to cyanogen chloride (NIOSH 1989; NRC 2002). Potential sources of occupational exposure to ammonium thiocyanate include the manufacture of electronic computing equipment, research and development laboratories, newspaper and other commercial printing, general medical and surgical hospitals, production of adhesives and sealants, and the construction and furniture industries (NIOSH 1989). Potential occupational exposures may also occur during the direct

5. POTENTIAL FOR HUMAN EXPOSURE

application of herbicidal formulations (e.g., amitrol-T, a mixture of ammonium thiocyanate and amino-1,2,4-triazole) and from handling, treatment, or disposal of thiocyanate-containing wastes from industrial processes (Brown and Morra 1993).

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

Table 5-1 summarizes information on companies that reported the production, import, or use of cyanide for the Toxics Release Inventory (TRI) in 2022 (TRI22 2024). TRI data should be used with caution since only certain types of industrial facilities are required to report. This is not an exhaustive list.

Table 5-1. Facilities that Produce, Process, or Use Cyanide Compounds

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
AK	3	100,000	999,999	1, 3, 5, 6, 10
AL	3	100	999,999	1, 3, 4, 5, 6, 12
AR	3	1,000	99,999	2, 3, 9, 12
AZ	2	1,000	999,999	1, 3, 10, 14
CA	5	0	999,999	1, 3, 5, 6, 10, 12
CO	1	100,000	999,999	1, 3, 5, 6, 10
GA	4	1,000	9,999	7, 10, 11, 12
IA	1	1,000	9,999	10
ID	2	1,000	99,999	1, 3, 7, 12
IL	17	100	99,999	1, 3, 5, 6, 7, 10, 12
IN	9	0	999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14
KY	4	0	99,999	1, 5, 6, 11, 14
LA	4	100	99,999	1, 5, 6, 12
MA	3	1,000	99,999	1, 2, 4, 6, 10, 12
ME	1	1,000	9,999	10
MI	9	0	999,999	1, 2, 3, 5, 6, 7, 10, 11, 12
MN	3	1,000	999,999	1, 3, 5, 6, 10
MO	6	1,000	99,999	1, 5, 6, 10, 11, 12, 14
MS	1	10,000	99,999	1, 5
NC	2	100	9,999	6, 7, 8, 10
NE	1	10,000	99,999	9, 12
NV	25	1,000	9,999,999	1, 3, 4, 5, 6, 9, 10, 11, 12, 13, 14
NY	2	1,000	9,999	6, 10, 14
OH	17	100	999,999	1, 3, 5, 6, 7, 8, 10, 11, 12, 13

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-1. Facilities that Produce, Process, or Use Cyanide Compounds

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
PA	4	0	999,999	1, 5, 10, 12, 13
PR	1	1,000	9,999	12
RI	4	100	9,999	1, 3, 4, 6, 7, 8, 10, 14
SC	5	100	999,999	1, 2, 3, 5, 8, 10, 11, 12, 13
SD	1	100,000	999,999	10
TN	3	10,000	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 10
TX	16	0	9,999,999	1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13
UT	3	1,000	99,999	1, 5, 7, 9, 11, 12
WI	5	100	999,999	1, 3, 5, 7, 10
WV	2	1,000	99,999	1, 5, 11, 14

^aPost office state abbreviations used.^bAmounts on site reported by facilities in each state.^cActivities/uses:

- | | | |
|----------------------|-----------------------------|--------------------------|
| 1. Produce | 6. Reactant | 11. Manufacture Aid |
| 2. Import | 7. Formulation Component | 12. Ancillary |
| 3. Used Processing | 8. Article Component | 13. Manufacture Impurity |
| 4. Sale/Distribution | 9. Repackaging | 14. Process Impurity |
| 5. Byproduct | 10. Chemical Processing Aid | |

Source: TRI22 2024 (Data are from 2022)

The Chemical Data Reporting (CDR) rule, under the Toxic Substances Control Act (TSCA), requires manufacturers (including importers) to provide EPA with information on the production and use of chemicals in commerce (EPA 2023a). Table 5-2 shows data for cyanide compounds from the 2020 national review.

Table 5-2. Nationally Aggregated Production Volume for Cyanide Compounds

Chemical name	2019	2018	2017	2016
Copper cyanide (CuCN)	100,000–<500,000	100,000–<500,000	100,000–<500,000	100,000–<500,000
Gold cyanide (AuCN)	145,715	139,809	145,226	159,878
Hydrocyanic acid	1,000,000,000–<5,000,000,000	1,000,000,000–<5,000,000,000	1,000,000,000–<5,000,000,000	1,000,000,000–<5,000,000,000
Potassium cyanide (KCN)	1,000,000–<20,000,000	1,000,000–<20,000,000	<1,000,000	1,000,000–<20,000,000

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-2. Nationally Aggregated Production Volume for Cyanide Compounds

Chemical name	2019	2018	2017	2016
Sodium cyanide (NaCN)	250,000,000– <500,000,000	250,000,000– <500,000,000	250,000,000– <500,000,000	250,000,000– <500,000,000

Source: EPA 2023a

There are two common methods of manufacturing hydrogen cyanide. The first method consists of the formation of hydrogen cyanide as a byproduct during the synthesis of acrylonitrile from the reaction of propylene and ammonia with air. The second method involves direct synthesis by the reaction of methane and ammonia with air over platinum catalysts, otherwise known as the Andrussow process (CMR 1993; Curry 1992; Homan 1987). Another less common manufacturing method, the Shawinigan process, has been applied in Spain and Australia and involves the reaction of ammonia with propane or butane in a fluidized bed of coke particles (Homan 1987; Shine 1971). Other methods of production include the dehydration of formamide and the reaction of sodium carbonate with coke-oven gas (Curry 1992; Sittig 1980). The predominant method of manufacture is the Andrussow process, which is used to make over 70% of the hydrogen cyanide; the remaining 30% is as a byproduct of acrylonitrile production (Maxwell et al. 2020).

The methods of commercial production of potassium and sodium cyanide include reacting potassium or sodium carbonate with carbon and ammonia, and reacting hydrogen cyanide with potassium or sodium hydroxide (Maxwell et al. 2020). Sodium cyanide can also be prepared by heating sodium amide with carbon or by melting sodium chloride and calcium cyanamide together in an electric furnace (Maxwell et al. 2020). Potassium silver cyanide is manufactured by adding silver chloride to a solution of potassium cyanide (Sax and Lewis 1987). Calcium cyanide is manufactured by heating calcium cyanamide with a source of carbon in electric furnaces at temperatures >1,000°C (Curry 1992; Homan 1987). It may also be produced by neutralization of lime with hydrogen cyanide (Homan 1987). As of 2009, no on-purpose calcium cyanide production facilities are operating (Maxwell et al. 2020).

Cyanogen is usually prepared by adding an aqueous solution of sodium or potassium cyanide to an aqueous solution of copper (II) sulfate or chloride (Homan 1987; Windholz 1983). It may also be produced by heating mercury cyanide or by heating hydrogen cyanide in the presence of a catalyst (Homan 1987). Cyanogen chloride is produced by the action of chlorine on hydrogen cyanide or by the action of chlorine on moist sodium cyanide suspended in carbon tetrachloride and kept cooled to -3°C

5. POTENTIAL FOR HUMAN EXPOSURE

(Homan 1987; Windholz 1983). Ammonium thiocyanate is produced by boiling an aqueous solution of ammonium cyanide with sulfur or polysulfides or by reaction of ammonia and carbon disulfide (Homan 1987; Sax and Lewis 1987).

5.2.2 Import/Export

The imports and exports of hydrogen cyanide through principal U.S. customs districts are negligible (CMR 2001). Import and export data for some of the cyanide compounds included in this profile are summarized in Table 5-3 for 2004 (USDOC 2004). Import volumes were greatest for thiocyanates, cyanates, and fulminates at 11.6 million pounds, followed by cyanides and cyanide oxides of sodium at 4.71 million pounds. China, Germany, Japan, Czech Republic, and the United Kingdom were the primary exporters of these cyanide chemicals to the United States in 2004 (USDOC 2004). Recent import data could not be found in the available literature for potassium silver cyanide, cyanogen, or cyanogen chloride.

Table 5-3. Import and Export Volumes of Cyanide Compounds in 2004^a

Compounds	Millions of pounds
Imports:	
Potassium cyanide	0.954
Calcium cyanide	0.006
Cyanides and cyanide oxides of sodium	4.71
Other cyanides and cyanide oxides	No data
Thiocyanates, cyanates, and fulminates	11.6
Exports:	
Potassium cyanide	3.82
Calcium cyanide	No data
Cyanides and cyanide oxides of sodium	147
Other cyanides and cyanide oxides	1.59
Thiocyanates, cyanates, and fulminates	1.56

^aUSDOC 2004

Cyanides and cyanide oxides of sodium comprise most exports for cyanide compounds with a volume of 147 million pounds. The second largest export item among the cyanide compounds was potassium cyanide at 3.82 million pounds. Export data could not be found in the available literature for calcium cyanide, potassium silver cyanide, cyanogen, or cyanogen chloride.

5. POTENTIAL FOR HUMAN EXPOSURE

5.2.3 Use

The predominant users of cyanides are the steel, electroplating, mining, and chemical industries. The principal cyanide compounds used in industrial operations are potassium and sodium cyanide and calcium cyanide, particularly in metal leaching operations (Curry 1992; EPA 1993). Cyanides have been well established in uses as insecticides and fumigants; in the extraction of gold and silver ores; in metal cleaning; in the manufacture of synthetic fibers, various plastics, dyes, pigments, and nylon; and as reagents in analytical chemistry (EPA 1978, 1993; Maxwell et al. 2020). Cyanides are present in some foods, but this presence is due mainly to the production of hydrogen cyanide from naturally-occurring cyanogenic compounds in foods (see Sections 5.5 and 5.6). Cyanogen has been used as a high-energy fuel in the chemical industry and as a rocket or missile propellant; cyanogen and its halides are used in organic syntheses, as pesticides and fumigants, and in gold-extraction processes (EPA 1978; Maxwell et al. 2020). When used in pesticidal applications and in accordance with the product label, cyanide compounds are registered and regulated by the EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (EPA 1998, 2004).

As a commercially available product, hydrogen cyanide is sold as a gas and is also available as a technical grade liquid in concentrations of 5, 10, and 96–99.5%. Almost all grades of hydrogen cyanide contain a stabilizer such as phosphoric acid to prevent decomposition and explosion (Curry 1992). In recent years, the use of hydrogen cyanide in the nylon and methyl methacrylate production processes has produced a strong demand (Maxwell et al. 2020). Estimates of worldwide uses for hydrogen cyanide in 2020 are as follows: adiponitrile for nylon (~28%); acetone cyanohydrin for acrylic plastics (~27%); sodium cyanide for gold, silver, and other metal recovery processes (~24%); methionine (Chemical Abstracts Service Registry Number [CASRN] 63-68-3) for animal feed (~10%); cyanuric chloride for pesticides and other agricultural products (~7%); and chelating agents such as ethylenediaminetetraacetic acid (EDTA) (~1%) (Maxwell et al. 2020).

Miscellaneous applications also include the use of hydrogen cyanide as an insecticide and rodenticide for fumigating enclosed spaces (grain storage, etc.) (Worthing 1987) and its use in the manufacture of ferrocyanides, acrylates, lactic acid, pharmaceutical, and specialty chemicals (Worthing 1987).

Cyanide salts have various uses. The most significant applications of compounds included in this profile are uses in electroplating and metal treatment, as an anti-caking agent in road salts, and in gold and silver extraction from ores. Minor applications include use as insecticides and rodenticides, as chelating agents,

5. POTENTIAL FOR HUMAN EXPOSURE

and in the manufacture of dyes and pigments (EPA 1978; Pesce 1993; Sax and Lewis 1987; Worthing 1987). Calcium cyanide is used as a cement stabilizer (Curry 1992; Windholz 1983) and has had limited use in rodent control and as a beehive fumigant (Lowe and Sullivan 1992). Formerly used as a polymerization catalyst and as an antifouling agent in marine paints, copper (I) cyanide continues to be used in plating baths for silver, brass, and copper-tin alloy plating (Maxwell et al. 2020).

The principal use of sodium cyanide is for the recovery of precious metals. Recovery of gold by cyanidation is the largest single mining use for sodium cyanide and has been growing owing to high gold prices (Maxwell et al. 2020).

Potassium cyanide is used for electrolytic refining of platinum; fine silver plating, as an electrolyte for the separation of gold, silver, and copper from platinum; and for metal coloring (Maxwell et al. 2020). One method of achieving hardened, weather-resistant metal surfaces uses a process known as cyaniding, which involves heating the metal in a liquid solution of sodium cyanide, sodium chloride, and sodium carbonate in the presence of atmospheric oxygen (Curry 1992). Fumigation of fruit trees, railway cars, and warehouses, and treatment of rabbit and rat burrows and termite nests are included among the former uses for sodium cyanide (Maxwell et al. 2020).

Cyanogen, a colorless gas with an almond-like odor, is used in organic syntheses, as a fumigant, as a fuel gas for welding and cutting heat-resistant metals, and as a rocket and missile propellant with ozone or fluorine (Sax and Lewis 1987). Applications of cyanogen chloride include use in chemical syntheses, as a military poison gas, as a metal cleaner, in ore refining, and in the production of triazine herbicides, optical brighteners, dyestuffs, and synthetic rubber (Hartung 1982; Homan 1987; Windholz 1983). Cyanogen chloride has also been used a warning agent in fumigant gases due to the fact that at low concentrations, it has strong lacrimatory effects (Homan 1987).

Ammonium thiocyanate is used as an ingredient in antibiotic fermentations, pesticides, liquid rocket propellants, adhesives, and matches; in photographic processes; to improve the strength of silks; in the manufacture of transparent artificial resins; and as a weed killer and defoliant (Sax and Lewis 1987; Weil et al. 2006; Windholz 1983).

5. POTENTIAL FOR HUMAN EXPOSURE

5.2.4 Disposal

Regulations governing the treatment and disposal of cyanide-containing wastes are detailed in Chapter 7. Cyanide is listed among the 65 toxic pollutants regulated by the Effluent Guidelines and Standards given in Title 40, Sections 400–475, of the Code of Federal Regulations (EPA 2023c). The pretreatment standards established for point source categories such as hydrogen peroxide manufacturing, electroplating, metal finishing, and ferroalloy manufacturing, regulate emissions of cyanides based on either total amount of cyanide or as cyanide that is amenable to chlorination in waste streams. Under the Resource Conservation and Recovery Act (RCRA), cyanide is listed as a hazardous waste when it is a discarded as a commercial chemical product, off-specification species, container residue, or spill residue; a waste from non-specific sources; or a waste from specific sources (EPA 1980). Eleven solid waste streams in the United States are classified as hazardous wastes under RCRA based on presence of cyanide salts and complexes (EPA 2023b). According to RCRA, cyanide-containing wastes are required to be treated by the best available technology before the wastes are disposed of in land. Cyanogen- and cyanogen-chloride-containing waste, for example, are assigned the hazardous waste codes P031 and P033, respectively, and must be treated by chemical or electrolytic oxidation employing specific oxidizing reagents (e.g., hypochlorite, peroxides, ozone, or ultraviolet light assisted ozone) or other reagents of equivalent efficiency; wet air oxidation incorporating a surrogate or indicator parameter; or treatment by incineration in units operated in compliance with RCRA standards (EPA 2023b). The concentration of cyanide permissible in wastes for land disposal is described in the Land Disposal Restriction in Title 40 Section 268, of the Code of Federal Regulations and varies according to the nature of wastes. The maximum concentration in treated waste (i.e., non-wastewater) should not exceed 590 mg/kg for total cyanides and 30 mg/kg for cyanides amenable to chlorination (EPA 1988). While liquids are prohibited from land disposal, the maximum concentrations allowable in most treated wastewaters, with the exception of the bottom streams from the acetonitrile column and the wastewater stripper used in the production of acrylonitrile, are 1.9 mg/L for total cyanides and 0.86 mg/kg for cyanides amenable to chlorination (EPA 1988).

Conducted in the presence of sodium hydroxide and sodium hypochlorite, the chemical oxidation method commonly referred to as alkaline chlorination is the most widely used commercial method for treating cyanide-containing wastes. This method results in the conversion of the cyanide solution to the less toxic cyanate. Depending on the cyanides present, the product will be a sludge or solution, which when sufficient reaction time has been allowed, will largely be devoid of free cyanide (IRPTC 1985).

5. POTENTIAL FOR HUMAN EXPOSURE

The alkaline chlorination process has been applied to the removal of cyanide from wastewaters and slurries generated as a consequence of cyanide heap leaching gold and other precious metals from low grade ores (EPA 1994). However, few mining sites currently use this technology. Instead, cyanide in wastewater or spent ore heaps is converted to cyanate through reactions with sulfur dioxide, ferrous sulfate, or hydrogen peroxide. These processes have been shown to effectively lower cyanide concentrations to levels that are within federal and state limits for discharge from the mining site (EPA 1994). A limitation of the technique is that it does not remove free chlorine, chloramines, or iron cyanides, which are toxic to fish. Other approaches that have demonstrated good efficiencies for removing cyanide from spent ore heaps and wastewater include precipitate from leachate through reaction with cuprous ions, reaction of cyanide ion with sulfur dioxide, or biodegradation of cyanide (Akcil and Mudder 2003; EPA 1994). The sulfur dioxide method is limited by an inability to remove thiocyanate, cyanate, and ammonia, which are toxic to fish, and may not provide sufficient removal efficiencies to meet local permit requirements (EPA 1994). Biodegradation of cyanide in wastewater and leachate is effective on soluble forms of cyanide, but may not be effective on degrading cyanide bound in metal complexes (EPA 1994).

Cyanide salts should not be treated with acid in preparation for disposal or flushed into drains that may contain, or subsequently receive, acid waste (IRPTC 1985). Similarly, incineration of cyanides must proceed with caution and is not recommended unless extensive equipment capable of safely handling liberated hydrogen cyanide is available (IRPTC 1985).

The biodegradation of cyanides has been investigated, with varying results, for several industrial processes, and additional research in this area would be valuable. While investigations of the potential for microbial species found in mineral processing wastewaters demonstrate effective removal of cyanide, metal complexed cyanide, and thiocyanate (Boucabeille et al. 1994b; EPA 1994), complex cyanides did not appear amenable to biodegradation at gasworks sites (Thomas and Lester 1993). Application of formaldehyde to electroplating waste under basic conditions can convert the cyanide anion to substituted acetates in addition to recovering copper and silver as free metals with formaldehyde reduction (Tucker and Carson 1985). Calcium or sodium polysulfide treatment converts some cyanide wastes into less toxic thiocyanate (Higgins and Desher 1988). These examples suggest that typical treatments involve the decomposition of cyanides to less toxic compounds by physical or chemical processes. More than 97% of cyanide is typically removed from wastewaters by alkaline chlorination, electrolysis, or ozonation processes (Grosse 1986). Cyanide from some wastes can be removed by ion-exchange resins. After using an appropriate treatment method such as those described above, cyanide wastes may be disposed of

5. POTENTIAL FOR HUMAN EXPOSURE

in a secured sanitary landfill (Grosse 1986; Higgins and Desher 1988; Tucker and Carson 1985). Disposal by injection of high-pH cyanide wastes into sandstone was investigated by Scrivner et al. (1986). The injection of wastewater containing hydrogen cyanide and cyanide compounds through underground injection is a major method for disposal of these wastes.

5.3 RELEASES TO THE ENVIRONMENT

The Toxics Release Inventory (TRI) data should be used with caution because only certain types of facilities are required to report (EPA 2022a). This is not an exhaustive list. Manufacturing and processing facilities are required to report information to the TRI only if they employ ≥10 full-time employees; if their facility's North American Industry Classification System (NAICS) codes is covered under EPCRA Section 313 or is a federal facility; and if their facility manufactures (defined to include importing) or processes any TRI chemical in excess of 25,000 pounds, or otherwise uses any TRI chemical in excess of 10,000 pounds, in a calendar year (EPA 2022a).

5.3.1 Air

Estimated releases of 137,365 pounds (~6.31 metric tons) of cyanide to the atmosphere from 17 domestic manufacturing and processing facilities in 2022, accounted for about 1.55% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). These releases are summarized in Table 5-4.

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Cyanide Compounds^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b							On- and off-site
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k	
AL	3	3,060	429	0	437,000	2,213	440,489	2,213	442,702
AK	3	0	45	0	160,042	0	160,086	0	160,086
AZ	2	384	0	0	263	0	647	0	647
AR	3	7	0	0	417,836	0	417,813	30	417,843
CA	5	0	1,525	0	1,392	0	200	2,717	2,917
CO	1	0	0	0	0	0	0	0	0
GA	4	30	5	0	0	0	35	0	35
ID	2	193	104	0	44	21	193	169	362

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Cyanide Compounds^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b							Total release	On- and off-site
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k		
IL	17	806	391	0	86	17,422	807	17,900	18,706	
IN	9	14	4,490	53,754	1,727	0	58,152	1,833	59,985	
IA	1	2	21	0	0	0	2	21	23	
KY	4	74,392	14	0	0	11	74,392	25	74,417	
LA	4	2	34	667,739	0	0	667,775	0	667,775	
ME	1	4	1	0	0	10,055	4	10,056	10,060	
MA	3	13	261	0	0	16,877	13	17,138	17,151	
MI	9	340	91	0	5	1	341	95	436	
MN	3	829	85	0	0	333	829	418	1,247	
MS	1	0	0	0	3	0	0	3	3	
MO	6	34	5	0	0	0	39	0	39	
NE	1	2	0	0	0	0	2	0	2	
NV	24	23,183	0	02,434,949	69	2,458,106	95	2,458,201		
NY	2	0	31	0	302	166	333	166	499	
NC	2	0	0	0	45	250	0	295	295	
OH	17	9,999	139	63,334	587	3,935	73,360	4,633	77,994	
PA	4	10,463	9,106	0	60	677,538	19,569	677,598	697,167	
RI	4	10	6	0	0	1,897	15	1,898	1,913	
SC	5	25	273	0	36,561	0	2,843	34,017	36,860	
SD	1	1,830	0	0	42	0	1,872	0	1,872	
TN	3	3,440	11,778	0	137	673	5,691	10,337	16,028	
TX	16	5,043	4,572	3,637,312	5,609	8,908	3,646,881	14,562	3,661,444	
UT	3	2,679	1,845	0	589	0	5,091	22	5,113	
WV	2	447	2,729	0	4,600	0	3,176	4,600	7,776	
WI	5	133	8	0	21,606	72	133	21,686	21,819	

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-4. Releases to the Environment from Facilities that Produce, Process, or Use Cyanide Compounds^a

State ^c	RF ^d	Reported amounts released in pounds per year ^b							Total release	
		Air ^e	Water ^f	UI ^g	Land ^h	Other ⁱ	On-site ^j	Off-site ^k	On- and off-site	
PR	1	0	0	0	0	0	0	0	0	0
Total	171	137,365	37,987	4,422,139	3,523,484	740,441	8,038,889	822,527	8,861,417	

^aThe TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.

^bData in TRI are maximum amounts released by each facility.

^cPost office state abbreviations are used.

^dNumber of reporting facilities.

^eThe sum of fugitive and point source releases are included in releases to air by a given facility.

^fSurface water discharges, wastewater treatment (metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).

^gClass I wells, Class II-V wells, and underground injection.

^hResource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.

ⁱStorage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown.

^jThe sum of all releases of the chemical to air, land, water, and underground injection wells.

^kTotal amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI22 2024 (Data are from 2022)

Vehicular emissions are the dominant source of urban ambient hydrogen cyanide. A 2016 report conservatively estimated that 654 tons of hydrogen cyanide were emitted in Canada in 2012 from light-duty vehicles (Moussa et al. 2016). In a 2007 study that estimated hydrogen cyanide emissions from motor vehicles in the South Coast Air Basin of California, hydrogen cyanide emissions from idling light-duty motor vehicles were estimated to be 4.9×10^{-3} tons/day (cold-start) (Baum et al. 2007).

EPA's National Emission Inventory (NEI) database contains information regarding sources that emit criteria air pollutants (CAPs) and their precursors, and hazardous air pollutants (HAPs) for the 50 United States, Washington DC, Puerto Rico, and the U.S. Virgin Islands. Emissions are estimated from multiple sources, including state and local environmental agencies; the TRI database; computer models for on- and off-road emissions; and databases related to EPA's Maximum Achievable Control Technology (MACT) programs to reduce emissions of HAPs. Cyanide emissions estimated from the 2017 inventory are summarized in Table 5-5.

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-5. Pounds of Cyanide Emitted by Sector

Emission sector	Pounds of cyanide emitted
Fuel combustion, commercial/institutional, coal	3,500
Fuel combustion, commercial/institutional, natural gas	7
Fuel combustion, commercial/institutional, oil	809
Fuel combustion, electric generation, coal	678,044
Fuel combustion, electric generation, natural gas	1,716
Fuel combustion, electric generation, oil	1
Fuel combustion, electric generation, other	740
Fuel combustion, industrial boilers, internal combustion engines, biomass	74
Fuel combustion, industrial boilers, internal combustion engines, coal	41,685
Fuel combustion, industrial boilers, internal combustion engines, natural gas	960
Fuel combustion, industrial boilers, internal combustion engines, other	94,047
Industrial processes, ferrous metals	7,947
Industrial processes, mining	98,805
Industrial processes, not elsewhere classified	82,089
Industrial processes, non-ferrous metals	42,673
Industrial processes, petroleum refineries	1,464,585
Industrial processes, pulp and paper	4,416
Industrial processes, storage and transfer	22,849
Miscellaneous non-industrial, not elsewhere classified	181,865
Solvent, degreasing	674
Solvent, dry cleaning	580
Solvent, graphic arts	581
Solvent, industrial surface coating and solvent use	3,646
Waste disposal	48,433

Source: EPA 2022b

5.3.2 Water

Estimated releases of 37,987 pounds (~17.23 metric tons) of cyanide to surface water from 17 domestic manufacturing and processing facilities in 2022, accounted for about 0.43% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). This estimate includes releases to wastewater treatment and publicly owned treatment works (POTWs) (TRI22 2024). These releases are summarized in Table 5-4.

5. POTENTIAL FOR HUMAN EXPOSURE

There are numerous sources that release cyanide into water. Cyanide is released into water from both point and nonpoint sources. The major point sources of cyanide released to water are discharges from POTWs, iron and steel production, and organic chemical industries (EPA 1981). Estimates based on data from the mid-to-late 1970s indicate that these sources account for ≈89% of the estimated 31 million pounds of total cyanide discharged annually to surface waters. Since metal finishing and organic chemical industries are estimated to account for 90% of the influent to POTWs, they are the dominant sources of both direct and indirect discharge of cyanide to water (EPA 1981). These data indicate that the industrial discharge of cyanides into surface water and POTWs decreased substantially in 1988 in comparison to the estimated discharge during the 1970s.

The effluents from the cyanidation process used in the extraction of precious metals from their ores may contain high levels of cyanide (Huiatt 1985; Korte and Coulston 1995; Mudder and Botz 2000; Scott 1985). The total cyanide content of typical tailing pond effluents from gold mill tailing ponds has been reported to range from 0.3 to 310 mg/L (EPA 1994; Scott 1985). Although the contribution from this source to the total discharge of cyanide into the environment has been estimated to be negligible on average (EPA 1981), large, short-term releases can occur from the failure of tailing ponds, resulting in the introduction of high concentrations of cyanide into local surface waters and subsoils (Fields 2001; Mudder and Botz 2000). Normally, these cyanide wastes undergo decontamination through the conversion of cyanide to the less toxic cyanate in a chemical oxidation method commonly referred to as alkaline chlorination. In the method, the cyanide wastes are treated with sodium hydroxide or sodium hypochlorite. Alkaline chlorination is the most widely used commercial method for treating cyanide-containing wastes. Depending on the cyanides present, the product will be a sludge or solution, which, when sufficient reaction time has been allowed, will, in time, largely be devoid of free cyanide (IRPTC 1985). Leachates from solid waste disposal sites are point sources of cyanide release to groundwater (Myers 1983; Venkataramani et al. 1984). No quantitative estimate of the amount of cyanide entering the groundwater from this point source was located. The nonpoint sources of cyanide released to water are comprised of agricultural and road runoff and atmospheric fallout and washout. The predominant sources of cyanides found in urban runoff samples were reported to be products of gasoline combustion and anticaking ingredients in road salts (Cole et al. 1984). Sodium ferrocyanide, which is used as an anticaking agent in road salts during the winter in the northeastern United States as well as Canada (AWI 2010; Exall et al. 2011), can potentially be washed off from roads into streams and storm sewers.

Thiocyanate is released to water primarily from discharges of industrial wastewaters from coal processing and extraction of gold and silver (Boucabeille et al. 1994a). Thiocyanate is also found in mining

5. POTENTIAL FOR HUMAN EXPOSURE

wastewaters where it results from the reaction of the cyanide anion (CN^-) with sulphur (Boucabeille et al. 1994b).

5.3.3 Soil

Estimated releases of 3,523,484 pounds (~1,598.23 metric tons) of cyanide to soil from 17 domestic manufacturing and processing facilities in 2022, accounted for about 39.76% of the estimated total environmental releases from facilities required to report to the TRI (TRI22 2024). An additional 4,422,139 pounds (~2,005.85 metric tons), constituting about 49.90% of the total environmental emissions, were released via underground injection (TRI22 2024). These releases are summarized in Table 5-4.

Estimates of amounts of cyanide released to soil from anthropogenic sources are limited. The largest anthropogenic sources of cyanide releases to soil probably result from the disposal of cyanide wastes in landfills and the use of cyanide-containing road salts (EPA 1981; Gaffney et al. 1987). In 77 of 124 hazardous waste sites in the United States, the median cyanide concentration in subsoil samples was 0.8 mg/kg (WHO 2004). In the same study, topsoil samples taken from 51 of 91 had median cyanide concentrations of 0.4 mg/kg. In the soils of former manufactured gas plant sites, the concentrations of cyanide compounds in the United States were <2,000 mg/kg (Shifrin et al. 1996; WHO 2004). The cyanides in these soils were predominantly (97%) in the form of ferrocyanides.

Natural biogenic processes of bacteria, fungi, and cyanogenic plants such as sorghum, soybeans, and cassava also release cyanide into the soil (EPA 1978; Knowles 1988; WHO 1992, 2004).

Releases of thiocyanate to soil result from anthropogenic and natural sources. Anthropogenic releases occur primarily from direct application in herbicidal formulations (e.g., amitrol-T, a mixture of ammonium thiocyanate and amino-1,2,4-triazole) and from disposal as byproducts from industrial processes. Nonanthropogenic sources include damaged or decaying tissues of plants from the family *Brassica* (e.g., mustard, rape) (Brown and Morra 1993).

5. POTENTIAL FOR HUMAN EXPOSURE

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

Air. Because hydrogen cyanide is a gas and has a relatively slow degradation rate in air (see Section 5.4.2), the atmosphere will be the ultimate sink for this compound. Almost all of the hydrogen cyanide released to the atmosphere remains in the lower altitudes (troposphere); only 2% of tropospheric hydrogen cyanide is transferred to the stratosphere (Cicerone and Zellner 1983). Cyanide has the potential to be transported over long distances from its emission source. Despite higher water solubility at saturated pressure, the removal of hydrogen cyanide by rainwater appears to be a negligible partitioning pathway (Cicerone and Zellner 1983). Because hydrogen cyanide is a gas, its removal from air by dry deposition is also likely to be negligible. However, metal cyanide particles, particularly water-soluble cyanide particles, are expected to be removed from the air by both wet and dry deposition.

Water. Volatilization and sorption are the two physical processes that contribute to the loss of cyanide from water. At pH <9.2, most of the free cyanide in solution should exist as hydrogen cyanide, a volatile cyanide form (EPA 1978). On the basis of Henry's law constant (see Table 4-2) and the volatility characteristics associated with various ranges of Henry's law constant (Thomas 1982), volatilization is a significant and probably dominant fate process for hydrogen cyanide in surface water (EPA 1992). The most common alkali metal cyanides (e.g., sodium and potassium cyanide) may also be lost from surface water primarily through volatilization, whereas the sparingly soluble metal cyanides such as copper (I) cyanide are removed from water predominantly by sedimentation and biodegradation (see Section 5.4.2) (EPA 1992). Variations in the volatilization rate are expected because this process is affected by several parameters including temperature, pH, wind speed, and cyanide concentration (EPA 1979). EPA (1979) summarized the unpublished results of a laboratory study that indicated that the volatilization half-life of hydrogen cyanide from solutions at concentrations of 25–200 µg/L ranged from 22 to 110 hours. First-order kinetics were observed. In outdoor experiments with moderate winds, the rate of hydrogen cyanide loss increased by a factor of 2–2.5 (EPA 1979). In a study to evaluate the effect of cyanide on biochemical oxidation, there was a 50% loss of 6 ppm (mg/L) cyanide in river water kept in open biochemical oxygen demand bottles (without aeration) at pH 7.4 within ≈10 days (Ludzack et al. 1951). When the bottles were aerated (rate of aeration not given), 50% loss occurred in only ≈10 hours. The kinetics of the rate of loss due to volatilization were not rigorously investigated. The volatilization rate was pH-dependent, with the rate faster at a lower pH. Data indicated that cyanide volatilization is a more important fate process than cyanide loss due to chemical and biodegradation reactions (see Section 5.4.2).

5. POTENTIAL FOR HUMAN EXPOSURE

(Ludzack et al. 1951; Raef et al. 1977a). Because volatilization is not an important fate process for cyanide in groundwater, cyanide would be expected to persist for considerably longer periods of time in underground aquifers than in surface water.

Sediment and Soil. Cyanides are sorbed by various natural media, including clays (Cruz et al. 1974), biological solids (Raef et al. 1977b), and sediments (EPA. 1979). However, additional data are necessary to assess the significance of cyanide sorption to suspended solids and sediments in water. Hydrogen cyanide and the alkali metal cyanides are not likely to be strongly sorbed onto sediments and suspended solids because of their high water solubilities (see Table 4-2). Soluble metal cyanides may show somewhat stronger sorption than hydrogen cyanide, with the extent of sorption increasing with decreasing pH and increasing iron oxide, clay, and organic material contents of sediment and suspended solids (EPA 1979). However, sorption is probably insignificant even for metal cyanides when compared to volatilization and biodegradation (EPA 1979, 1992).

Other Media. There are no data available to indicate that simple metal cyanides and hydrogen cyanide bioconcentrate in aquatic organisms (EPA 1979, 1980, 1985a, 1992). Bioconcentration factors (BCFs) of 0.73 and 1.62 can be calculated for hydrogen cyanide, using the equation of Veith et al. (1979) for the BCF of a chemical in whole fish ($\log \text{BCF}$, 0.85; $\log K_{\text{ow}}$, -0.70) and the $\log K_{\text{ow}}$ values in Table 4-2. Similarly, the calculated BCF for sodium cyanide is 0.47. There is some evidence that certain metal cyanide complexes bioaccumulate in aquatic organisms. Fish from water with soluble silver and copper cyanide complexes were found to have metal cyanides in their tissues at concentrations ranging up to 168 and 304 $\mu\text{g/g}$, respectively (wet or dry weight not specified) (EPA 1979). It is difficult to evaluate the toxicologic significance of bioaccumulation of metal cyanide complexes because these compounds are much less toxic than soluble hydrogen cyanide, sodium cyanide, or potassium cyanide (EPA 1992). There is no evidence of biomagnification of cyanides in the food chain (EPA 1978). Accumulation of cyanide in food webs is not expected, considering the rapid detoxification of cyanide by most species and the lethal effects of large doses of cyanide (EPA 1978).

Volatilization of hydrogen cyanide would be a significant loss mechanism for cyanides from soil surfaces at a pH <9.2. Cyanides are fairly mobile in soil. Mobility is lowest in soils with low pH and high concentrations of free iron oxides, positively charged particles, and clays (e.g., chlorite, kaolin, gibbsite), and highest in soils with high pH, high concentrations of free CaCO_3 and negatively charged particles, and low clay content (EPA 1979). Although cyanide has a low soil sorption capability, it is usually not detected in groundwater, probably because of fixation by trace metals through complexation or

5. POTENTIAL FOR HUMAN EXPOSURE

transformation by soil microorganisms (see Section 5.4.2) (EPA 1978). In soils where cyanide levels are high enough to be toxic to microorganisms (i.e., landfills, spills), this compound may leach into groundwater (EPA 1984). Also, leaching of cyanide into a shallow aquifer can occur, as demonstrated by the high concentration of cyanide (1,200 µg/L) in groundwater sampled from the Biscayne Aquifer in Dade County, Florida, which lies below a solid waste site (Myers 1983).

No information could be found in the available literature on the transport and partitioning of cyanogen chloride in the environment, or its partitioning coefficients (K_{oc} , K_{ow}) or Henry's law constants (see Table 4-2). Like cyanogen, cyanogen chloride is a highly volatile gas (see Table 4-2). Therefore, it would be expected that volatilization from water and soil would be a primary route of environmental partitioning for both cyanogen and cyanogen chloride.

Similarly, little information could be found in the available literature on the environmental transport and partitioning of thiocyanate in the environment. At near ambient temperatures ($\approx 30^{\circ}\text{C}$), it appears that sorption and volatilization are not significant partitioning processes for thiocyanate in soil, with thiocyanate losses due primarily to microbial degradation (see Section 5.4.2) (Brown and Morra 1993).

5.4.2 Transformation and Degradation

The various cyanide compounds included in this profile undergo a number of different transformation and degradation reactions in the environment as discussed in the following sections. The resulting environmental transformation products within different media are shown in Table 5-6.

Table 5-6. Environmental Transformation Products of Cyanide Compounds by Medium

Parent compound	Product(s)	Comments	Reference
Air			
HCN	HO CN + HO ₂ (unlikely)	HNC-OH intermediate	Cicerone and Zellner 1983
	NO + CHO ⁻ (formed in minutes)	HCN-OH intermediate	Cicerone and Zellner 1983
Cyanogen	HCN, NCOH, and other compounds	In the presence of water; slow reaction	EPA 1979

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-6. Environmental Transformation Products of Cyanide Compounds by Medium

Parent compound	Product(s)	Comments	Reference
Water			
HCN	$\text{NH}_4^+ + \text{HCOO}^-$ in equilibrium with $\text{H}_2\text{NCHO} + \text{H}_2$	pH dependent (pH < 1, half-life: 10–1,000 hours)	EPA 1979
	$\text{NH}_4^+ + \text{HCOO}^-$	Alkaline hydrolysis; very slow reaction	
CN^-	Metal cyanides	In the presence of excess metals; alkali metal cyanides very soluble; alkaline earth metal cyanides not very soluble	EPA 1979, 1992
	Complex metallocyanides	Excess CN^- in the presence of metals; solubilities of metallocyanides vary	EPA 1979, 1992
	>99% HCN	pH < 7	EPA 1978
	$\text{NH}_3 + \text{CO}_2$ (NH_3 converted to nitrite and nitrate in presence of nitrifying bacteria)	Aerobic biotransformation	Richards and Shieh 1989
	$\text{N}_2 + \text{CO}_2$	Anaerobic biotransformation under denitrification conditions	Richards and Shieh 1989
HCN/CN ⁻ salts	SCN^- , $\text{NH}_3 + \text{CO}_2$, CHOO^-	Biotransformation	EPA 1978
Cyanogen	HCN, NCOH, and other compounds	Slow reaction at pH 7; 5.25 hours at pH 8.5	EPA 1979; Munro et al. 1999; U.S. Army 1989
Metallocyanides	CN^- (possibly)	Photolysis	EPA 1979
	OCN^-	Oxidation	EPA 1992
	$\text{CO}_2 + \text{N}_2$	In the presence of strong oxidizing agents	EPA 1992
SCN ⁻	HCN	In acidic media	EPA 1979
Sediment and soil			
CN^-	Metallocomplexes	Abiotic transformation in the presence of metals	EPA 1978
	$\text{NH}_3 + \text{CO}_2$ (NH_3 converted to nitrite and nitrate in presence of nitrifying bacteria)	Aerobic biotransformation (predicted from fate in wastewater)	Richards and Shieh 1989
	$\text{N}_2 + \text{CO}_2$	Aerobic biotransformation under denitrification conditions (predicted from fate in wastewater)	Richards and Shieh 1989
SCN ⁻	COS (possibly; microbial degradation pathway not known)	Microbial degradation	Brown and Morra 1993

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-6. Environmental Transformation Products of Cyanide Compounds by Medium

Parent compound	Product(s)	Comments	Reference
Wastewater/sludge			
CN ⁻	NH ₃ + CO ₂ (NH ₃ converted to nitrite and nitrate in presence of nitrifying bacteria)	Aerobic biotransformation	Richards and Shieh 1989
	N ₂ + CO ₂	Anaerobic biotransformation under denitrification conditions	Richards and Shieh 1989
CN ⁻ /metallocyanides (including cuprocyanide)	NH ₃ + CO ₂	Microbial degradation in mining wastewaters	Boucabeille et al. 1994b
SCN ⁻	NH ₃ + CO ₂ + SO ₄	Microbial degradation in mining wastewaters	Boucabeille et al. 1994a
	COS + NH ₃	Microbial degradation in activated sludge	Katayama et al. 1993

CHO⁻ = carbonyl ion; CHOO⁻ = formate ion; CN⁻ = cyanide anion; CO₂ = carbon dioxide; COS = carbonyl sulfide; H₂ = hydrogen gas; H₂NCHO = formamide; HO₂ = hydroperoxyl radical; HCN = hydrogen cyanide; HNC = hydrogen isocyanide; HOCl = cyanic acid; N₂ = nitrogen gas; NCOH = cyanic acid; NH₃ = ammonia; NO = nitric oxide; OCN⁻ = isocyanate; OH = hydroxide; SCN⁻ = thiocyanate; SO₄ = sulfate

Air. Most cyanide in the atmosphere exists almost entirely as hydrogen cyanide gas, although small amounts of metal cyanides may be present as particulate matter in the air (EPA 1984). Hydrogen cyanide is very resistant to photolysis at wavelengths of normal sunlight (EPA 1979). The most important reaction of hydrogen cyanide in air is the reaction with photochemically-generated hydroxyl radicals and subsequent rapid oxidation to carbon monoxide (CO) and nitric oxide (NO); photolysis and reaction with ozone are not important transformation processes, and reaction with singlet oxygen (O¹D) is not a significant transformation process except at stratospheric altitudes where singlet oxygen is present in significant concentrations (Cicerone and Zellner 1983). The rate of hydroxyl radical reaction with hydrogen cyanide in the atmosphere depends on the altitude, and the rate of the reaction is at least an order of magnitude faster at lower tropospheric altitudes (0–8 km) than at upper tropospheric altitudes (10–12 km) (Cicerone and Zellner 1983). Based on a reaction rate constant of 3×10⁻¹⁴ cm³/(molecule-second) at 25°C (Fritz et al. 1982) and assuming an average hydroxyl radical concentration of 5×10⁵ molecules/cm³, the residence time for the reaction of hydrogen cyanide vapor with hydroxyl radicals in the atmosphere is ≈2 years. This value compares well with the atmospheric residence time derived by Cicerone and Zellner (1983) of approximately 2.5 years, with a range of 1.3–5.0 years, depending on the hydroxyl radical concentrations assumed. Using the equation t_½=0.693τ for converting residence time (τ) to half-life (t_½) (Lyman 1982) and an estimated atmospheric residence time for

5. POTENTIAL FOR HUMAN EXPOSURE

hydrogen cyanide of 2–3 years, and assuming first-order kinetics for the reaction of hydrogen cyanide with hydroxyl radicals, an atmospheric half-life of 1.4–2.9 years can be calculated for hydrogen cyanide.

Cyanogen is reactive and does not persist in the environment unchanged (EPA 1978). Cyanogen reacts slowly with water to yield hydrogen cyanide and cyanic acid (HOCl) among other products (EPA 1979) and this hydrolysis reaction may be a possible atmospheric degradation pathway. Cyanogen has also been shown to react with hydroxyl radicals in the gas phase (Atkinson 1989). Based on a rate constant of $2.5 \times 10^{-15} \text{ cm}^3/(\text{molecule-second})$ at 27°C and assuming an average hydroxyl radical concentration of $5 \times 10^5 \text{ molecules/cm}^3$, the residence time for the reaction of hydrogen cyanide vapor with hydroxyl radicals in the atmosphere is ≈25 years. Therefore, the reaction of cyanogen with photochemically induced hydroxyl radicals will not play a significant role in the degradation of this compound in air.

No specific information was found in the available literature on the transformation and degradation of cyanogen chloride or thiocyanates in air. However, cyanogen chloride has been shown to undergo slow hydrolysis in neutral aqueous solution (rate constant at pH 7 of $6.45 \times 10^{-5} \text{ molecules}^{-1}\text{second}^{-1}$) (U.S. Army 1989). Therefore, hydrolysis of this compound may be a possible atmospheric degradation pathway in air.

Water. Cyanide occurs most commonly as hydrogen cyanide in water, although it can also occur as the cyanide ion, alkali and alkaline earth metal cyanides (potassium cyanide, sodium cyanide, calcium cyanide), relatively stable metallocyanide complexes (ferricyanide complex $[\text{Fe}(\text{CN})_6]^{3-}$), moderately stable metallocyanide complexes (complex nickel and copper cyanide), or easily decomposable metallocyanide complexes (zinc cyanide $[\text{Zn}(\text{CN})_2]$, cadmium cyanide $[\text{Cd}(\text{CN})_2]$). The environmental fate of these cyanide compounds varies widely (EPA 1979).

Oxidation, hydrolysis, and photolysis are the three predominant chemical processes that may cause loss of simple cyanides in aquatic media. Certain cyanides are oxidized to isocyanates by strong oxidizing agents; the isocyanates may be further hydrolyzed to ammonia and carbon dioxide (EPA 1978). However, it has not yet been determined whether such oxidation and subsequent hydrolysis of isocyanate is a significant fate process in natural waters known to contain peroxy radicals (EPA 1992).

In water, hydrogen cyanide and cyanide ion exist in equilibrium with their relative concentrations primarily dependent on pH and temperature. At pH <8, >93% of the free cyanide in water will exist as undissociated hydrogen cyanide (EPA 1978). Hydrogen cyanide can be hydrolyzed to formamide, which

5. POTENTIAL FOR HUMAN EXPOSURE

is subsequently hydrolyzed to ammonium and formate ions (EPA 1979). However, the relatively slow rates of hydrolysis reported for hydrogen cyanide in acidic solution (Krieble and McNally 1929; Krieble and Peiker 1933) and of cyanides under alkaline conditions (Wiegand and Tremelling 1972) indicate that hydrolysis is not competitive with volatilization and biodegradation for removal of free cyanide from ambient waters (EPA 1979).

The alkali metal cyanides are very soluble in water. As a result, they readily dissociate into their respective anions and cations when released into water. Depending on the pH of the water, the resulting cyanide ion may then form hydrogen cyanide or react with various metals in natural water. The proportion of hydrogen cyanide formed from soluble cyanides increases as the water pH decreases. At pH <7, >99% of the cyanide ions in water are converted to hydrogen cyanide (EPA 1978). As the pH increases, cyanide ions in the water may form complex metallocyanides in the presence of excess cyanides; however, if metals are prevalent, simple metal cyanides are formed. Unlike water-soluble alkali metal cyanides, insoluble metal cyanides are not expected to degrade to hydrogen cyanide (EPA 1979).

The significance of photolysis in the fate of cyanides in water has not been fully investigated. Hydrogen cyanide and cyanide ions in aqueous solution have been found to be very resistant to photolysis by natural sunlight, except under heterogeneous photocatalytic conditions (EPA 1979; Frank and Bard 1977). Photocatalytic oxidation may not be significant in natural waters, however, because of significant light reduction at increasingly greater depths (EPA 1992). In clear water or at water surfaces, some metallocyanides, such as ferrocyanides and ferricyanides, may decompose to the cyanide ion by photodissociation and subsequently form hydrogen cyanide. For example, diurnal changes in free cyanide concentrations in the drainage from spent precious metal ore heaps were found to maximize around mid-day due to the photodissociation of iron and cobalt cyanocomplexes (Johnson et al. 2002). Because of adsorption of ferrocyanide onto soil surfaces and sediment of surface waters, and light scattering in turbid waters in the field, the rate of free cyanide formation from the photolysis of ferrocyanide in runoff and surface water from washout of ferrocyanide in de-icing salt will be slower than from laboratory photolysis with clean water (EPA 1979).

Biodegradation is an important transformation process for cyanide in natural surface waters, and is dependent on such factors as cyanide concentrations, pH, temperature, availability of nutrients, and acclimation of microbes. Although the cyanide ion is toxic to microorganisms at concentrations as low as 5–10 mg/L (Klecka et al. 1985; Malaney et al. 1959), acclimation increases tolerance to this compound (Raef et al. 1977a). A number of pure cultures of microorganisms degrade low concentrations of cyanide

5. POTENTIAL FOR HUMAN EXPOSURE

under both aerobic and anaerobic conditions (EPA 1978, 1979, 1992). However, biodegradation data derived from use of a pure culture are not strictly relevant to natural waters that contain mixed cultures. Mixed microorganisms in sewage sludge or activated sludge acclimated to cyanide also significantly biodegrade concentrations ≤ 100 mg/L of most simple and complex cyanides (Gaudy et al. 1982; Pettet and Mills 1954; Richards and Shieh 1989; Shivaraman et al. 1985). In a study to evaluate the effect of the cyanide ion on biochemical oxidation conducted in sealed vessels, a 50% loss of cyanide at concentrations ≤ 6 mg/L in two natural river waters occurred at times estimated to range from <10 to 24 days (Ludzack et al. 1951). The rate of loss appeared to be linear within this time frame. These data may represent a biodegradation half-life; however, the possibility of loss by chemical reaction was not addressed in this study.

Most of the available information on the mechanisms of biodegradation of cyanides in water comes from studies on the evaluation and use of this process as a means of detoxifying cyanide-containing wastes (Akcil and Mudder 2003; EPA 1994; Raybuck 1992). It is known that there is a natural attenuation of the cyanide ion and thiocyanide concentrations in wastewaters (e.g., gold mill tails) due to acclimation of indigenous microflora in the tailings (Akcil and Mudder 2003; Oudjehani et al. 2002; Zagury et al. 2004). A number of microorganisms have been identified that are capable of uptake, conversion, sorption, and/or precipitation of the cyanide ion, cyanate, and thiocyanate, including species of the genera, *Actinomyces*, *Alcaligenes*, *Arthrobacter*, *Bacillus*, *Micrococcus*, *Neisseria*, *Paracoccus*, *Pseudomonas*, and *Thiobacillus* (Akcil and Mudder 2003). Some of these species (e.g., *Pseudomonas*) are capable of using the cyanide ion and thiocyanate as the sole source of carbon and nitrogen and are therefore particularly effective at cyanide degradation. In fact, *Pseudomonas* is the basis of commercial applications for degrading the cyanide ion to ammonia and carbonate in wastewaters generated in mining operations that use the cyanide ion to leach gold and other precious metals for low-grade ores (Akcil and Mudder 2003).

Raybuck (1992) reviewed the role of microbes in cyanide degradation and categorized the microbial enzymes that use the cyanide ion as a substrate according to the following types of reactions: substitution/addition, hydrolysis, oxidation, and reduction. Sulfur transferases such as rhodanese are involved in substitution reactions that result in the conversion of the cyanide ion to the less toxic thiocyanate, whereas pyridoxal phosphate enzymes are involved in substitution/addition reactions that result in production of nitrile derivatives of α -amino acids. These organic nitriles may then be ultimately degraded via enzyme catalyzed hydrolysis to either the corresponding amino acid and ammonia (without formation of the free amide) or the carboxylic acid and ammonia (via formation of the free amide). The cyanide hydratase and cyanidase enzymes catalyze the hydrolysis of the cyanide ion to formamide or

5. POTENTIAL FOR HUMAN EXPOSURE

formic acid and ammonia, respectively. A strain of *Alcaligenes xylosoxidans subsp. denitrificans* has been found to effectively hydrolyze the cyanide ion concentrations up to 300 mg/L down to very low levels (0.01–0.02 mg/L) and to be resistant to inactivation by chloride, sulfate, iodide, Fe^{+2} , Zn^{+2} , or Ni^{+2} at concentrations of 70 mg/L (Basheer et al. 1992). Thus, these hydrolytic systems are some of the most promising for detoxification of cyanide-containing wastewaters (Raybuck 1992). A number of microbial systems have been identified that are capable of direct oxidation or reduction of the cyanide ion. *Bacillus pumulus*, *Pseudomonas fluorescens*, and *Pseudomonas paucimobili* have all been found to oxidize the cyanide ion to ammonia and carbon dioxide (Meyers et al. 1993). In an aerobic batch bioreactor experiment, *Pseudomonas putida* was found to significantly degrade 4 mM sodium cyanide (cyanide concentration approximately 100 mg/L) to ammonia and carbon dioxide (Chapatwala et al. 1993). Other evidence indicates that formamide and formate are additional transformation products in microbial oxidation of the cyanide ion by this species, inferring that there may be more than one pathway of cyanide biotransformation involved (Kunz et al. 1992; White et al. 1988). Several bacterial species have been identified that are capable of oxidative degradation of metallocyanides (Silva-Avalos et al. 1990). The cyanide oxygenase system involved in this process offers a new technology for the treatment of metal cyanide wastes (Raybuck 1992).

The ferrocyanide complex is not easily biodegradable (Belly and Goodhue 1976; Pettet and Mills 1954). However, when an aqueous solution of potassium ferrocyanide was seeded with pure culture of *Pseudomona aeruginosa*, or *E. coli*, or a mixture of the two bacteria, formation of free cyanide was observed after a delay period of ≈2 days (Cherryholmes et al. 1985). The rate of free cyanide formation, when measured as CN^- , increased with addition of nutrient in water, and a free cyanide concentration $\leq 4,000 \mu\text{g/L}$ was detected at the end of 25 days. It was shown that the free cyanide formation was due to biodegradation and not to either photolysis or hydrolysis. The relevance of this study to the fate of ferrocyanide complexes in natural water or industrial effluents is difficult to assess because ferrocyanide concentrations used in these experiments (3,300 mg/L) are rarely encountered in these media.

Biodegradation is also a significant transformation process for thiocyanates in natural waters; however, additional data are needed to assess the relative importance of this process. Like the cyanide ion, thiocyanate is toxic to microorganisms at high concentrations and acclimated cultures have increased tolerance to this compound (Boucabeille et al. 1994a). Laboratory studies have shown that at concentrations up to at least 1.42 g/L, thiocyanate was completely degraded within 4 days to ammonia and sulfate ion (SO_4^{2-}) by an acclimatized co-culture of two bacteria (*Acinetobacter johnsonii* and

5. POTENTIAL FOR HUMAN EXPOSURE

Pseudomonas diminuta) isolated from sludge from an urban sewage treatment plant (Boucabeille et al. 1994a). Thiosulfate ion ($S_2O_3^{2-}$) was identified as the intermediate in this degradation pathway.

Several studies document the biodegradation of mixtures of cyanides and thiocyanate in wastewaters (e.g., Akcil and Mudder 2003; Boucabeille et al. 1994b; EPA 1994; Mudder and Whitlock 1984; Paruchuri et al. 1990; Shivaraman et al. 1985). Under aerobic conditions, the biodegradation of the cyanide ion and thiocyanate initially produces ammonia, which is converted to nitrite and nitrate in the presence of nitrifying bacteria, whereas anaerobic biodegradation under denitrification conditions may produce nitrogen (Richards and Shieh 1989). Complete biodegradation of simple and metal complexed cyanides and thiocyanate from mining wastewaters by various bacteria belonging to the families *Pseudomonadaceae*, *Vibrioniaceae*, and *Enterobacteriaceae* has been reported (Boucabeille et al. 1994b). Biodegradation of cyanide and thiocyanate resulted in the formation of ammonia, with or without accumulation of nitrite and/or nitrate, depending on whether a batch, fed-batch, or continuous treatment process was used. Sulphate ions were produced from thiocyanate degradation. Shivaraman et al. (1985) reported the uninhibited microbial degradation of thiocyanate and the cyanide ion to ammonia by acclimatized mixed cultures at cyanide concentrations up to 22.40 ± 1.34 mg/L, whereas Paruchuri et al. (1990) reported the complete inhibition of microbial degradation of thiocyanate in the presence of 10 mg/L cyanide ion.

Cyanogen reacts slowly with water to produce hydrogen cyanide, cyanic acid, and other compounds (EPA 1979). Cyanogen chloride also hydrolyzes slowly to cyanic acid and hydrochloric acid in water at pH 7, with a rate constant of 6.45×10^{-5} molecules $^{-1}$ second $^{-1}$ (U.S. Army 1989). Hydrolysis of cyanogen chloride is more rapid under acidic and basic conditions, with rate constants of 2×10^{-2} and $6 - 8 \times 10^{-2}$ molecules $^{-1}$ second $^{-1}$ (pH 10), respectively (U.S. Army 1989). The half-life of cyanogen chloride at neutral pH ranges between 1 minute at 45°C and 10 hours at 5°C (Opresko et al. 1998). However, volatilization would be expected to be the predominant fate process for both cyanogen chloride and cyanogen in water and, therefore, these compounds are not expected to persist in water.

Sediment and Soil. Analogous to the fate of cyanides in water, it is predicted that the fate of cyanides in soil would be dependent on cyanide concentrations, pH, temperature, metal content, concentration of microbes, availability of nutrients, and acclimation of microbes. Cyanide may occur as hydrogen cyanide, alkali metal salts, or as immobile metallocyanide complexes. In soil, cyanide present at low concentrations would biodegrade under aerobic conditions with the initial formation of ammonia, which would be converted to nitrite and nitrate in the presence of nitrifying bacteria. Under anaerobic

5. POTENTIAL FOR HUMAN EXPOSURE

conditions, the cyanides ion will denitrify to gaseous nitrogen (Richards and Shieh 1989). Upper limits of 200 and 2 ppm (mg/kg CN⁻), respectively, have been reported for uninhibited aerobic and anaerobic biodegradation of cyanide in soil (Fuller 1985); however, these limits have not been confirmed in other studies (Thomas and Lester 1993). Cyanide ions in soil are not involved in oxidation-reduction reactions but may undergo complexation reactions with metal ions in soil (EPA 1978).

No information was found in the available literature on the transformation of cyanogen or cyanogen chloride in soil or sediment. However, because these compounds are highly volatile gases, they are not expected to persist in soils. Additionally, biotic or abiotic degradation would not be expected to be significant fate processes compared to volatilization.

Although the fate of thiocyanate in soil is largely uncharacterized, there is evidence to suggest that thiocyanate is not persistent in soils. Early studies have shown that thiocyanate can undergo both aerobic (Betts et al. 1979) and anaerobic microbial degradation (Betts et al. 1979; Stafford and Callely 1969; Youatt 1954); however, the degradation pathway has not been defined (Brown and Morra 1993). Saturated soils treated with thiocyanate were found to emit carbonyl sulfide (Minami 1982; Minami and Fukushi 1981). Katayama et al. (1992, 1993) reported the formation of carbonyl sulfide from the biodegradation of thiocyanate by pure and mixed cultures of *Thiobacillus thioparus*. These species are ubiquitous in soil (Kelly and Harrison 1989). In a laboratory investigation of the fate of ionic thiocyanate in six different soils, Brown and Morra (1993) concluded that microbial degradation is the primary mechanism for thiocyanate disappearance at $\leq 30^{\circ}\text{C}$, with carbonyl sulfide proposed as a possible hydrolysis product. Loss of thiocyanate at higher temperatures ($50\text{--}60^{\circ}\text{C}$) did not appear to result from microbial degradation; the observed decreases in thiocyanate concentrations of soil extracts with incubation time at elevated temperatures were postulated to result primarily from increased sorption or increased sorption kinetics, but abiotic catalysis of thiocyanate degradation was also noted as a possible cause.

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to cyanide depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of cyanide in unpolluted atmospheres and in pristine surface waters are often so low as to be near the limits of current analytical methods. In reviewing data on cyanide levels monitored or estimated in the

5. POTENTIAL FOR HUMAN EXPOSURE

environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

Table 5-7 shows the lowest limit of detections that are achieved by analytical analysis in environmental media. An overview summary of the range of concentrations detected in environmental media is presented in Table 5-8.

Table 5-7. Lowest Limit of Detection for Cyanide Anion based on Standards^a

Media	Detection limit	Reference
Air	0.16 ppbv	Zain et al. 2017
Drinking water	0–0.5 ppb	EPA 2020
Surface water and groundwater	0.5 ppb	EPA 2020
Soil	0.2 ppm	EPA 2014
Sediment	0.2 ppm	EPA 2014

^aDetection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

Table 5-8. Summary of Environmental Levels of Cyanide

Media	Low	High	For more information
Outdoor air (ppbv)	0.16	0.76	Section 5.5.1
Indoor air (ppmv)	1.8	320	Section 5.5.1
Surface water (ppb)	<1	444	Section 5.5.2
Groundwater (ppb)	No data	>200	Section 5.5.2
Drinking water (ppm)	<1	50	Section 5.5.2
Food (ppm)	0.001	1,515	Section 5.5.5
Soil (ppm)	0.32	70.55	Section 5.5.3

Detections of cyanide in air, water, and soil at NPL sites are summarized in Table 5-9.

Table 5-9. Cyanide Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median ^a	Geometric mean ^a	Geometric standard deviation ^a	Number of quantitative measurements	NPL sites
Cyanide					
Water (ppb)	123	236	24.1	138	86
Soil (ppb)	24,100	26,500	26.8	140	84

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-9. Cyanide Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median ^a	Geometric mean ^a	Geometric standard deviation ^a	Number of quantitative measurements	NPL sites
Air (ppbv)	26.2	64.2	6.5	4	2
Hydrogen cyanide					
Water (ppb)					
Soil (ppb)					
Air (ppbv)	990	1,250	1.5	3	2

^aConcentrations found in ATSDR site documents from 1981 to 2022 for 1,868 NPL sites (ATSDR 2022a). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

Recently reported concentrations of cyanide in outdoor range from 0.33 to 0.76 ppbv (Jaszczak et al. 2017). The high value of 0.76 ppbv was found near a gold heap leach field. For indoor air, levels of 320 ppmv (vehicular exposure in a garage), 14–20 ppmv (air in a car), and 1.8 ppmv (after a fire) were reported (Jaszczak et al. 2017).

Historical air concentrations of hydrogen cyanide in the northern hemisphere's non-urban troposphere ranged from 0.16 to 0.166 ppbv (Cicerone and Zellner 1983; Jaramillo et al. 1989). Semi-quantitatively measured hydrogen cyanide concentrations in the offgas from shale oil retorting processes measured from 1977 and 1980 were 6–39 ppmv in one retort at one site; however, hydrogen cyanide was not detected in retorts at another site (Sklarew and Hayes 1984).

5.5.2 Water

The WQP is a source of discrete water-quality data in the United States and beyond (WQP 2024). This cooperative service integrates publicly available water-quality data from the USGS, EPA, and over 400 state, federal, tribal, and local agencies. Analysis of compiled data from the WQP that spans 4 decades (1981–2023) indicates that cyanide is a common water pollutant. Of 1178,204 samples analyzed, cyanide was detected in 67,266 (37.8% of samples). Of those 67,266 samples, only 688 had values >10 µg/L. There were 91 drinking/potable water samples found, with values between 10 and 50 µg/L. Cyanide levels were below the level of detection (1.0 µg/L) in drinking water samples from

5. POTENTIAL FOR HUMAN EXPOSURE

Sunnyvale, San Jose, and Twain Harte Valley, California in the early 2000s (Christison and Rohrer 2007). Surface water samples in nearby mining areas (Twain Harte Valley and Alamitos Creek) also showed cyanide levels below the level of detection. Data from 1993–1998 indicated that only 0.2% of public water systems using groundwater exceeded the maximum contaminant level (MCL) of 0.2 mg/L (EPA 1999).

In a study that measured cyanide in urban snowmelt and runoff from deicer (which contains ferricyanide) in Canada, values were detected between 1 and 444 µg/L for weakly dissociable cyanide (Exall et al. 2011). Cyanide concentrations in run-off obtained from an area that had been burned in a 2000 wildfire that occurred in Tennessee and North Carolina near the Smokey Mountains National Park averaged 49 µg/L (Barber et al. 2003). This is equal to the LC₅₀ for cyanide in rainbow trout and is more than an order magnitude greater than the cyanide concentration measured in run-off obtained from unburned areas surrounding the wildfire site. Higher cyanide concentrations were reported in run-off from the Cerro Grande fire that occurred near Los Alamos, New Mexico in 2000 with an average value of 80 µg/L.

Cyanogen chloride is formed in drinking water from the reaction of humic substances with chloramine used during chlorination (Jacangelo et al. 1989; Ohya and Kanno 1987; WHO 2007). No recent data on levels of cyanogen chloride in drinking water were found in the available literature. In a mid-1970s EPA survey, cyanogen chloride was detected in drinking water from 8 of 10 U.S. cities (Fielding and Packham 1977). The use of chloramine as a final disinfectant produces levels of cyanogen chloride that are 4–15 times higher than levels produced when chlorine is used (Jacangelo et al. 1989; Krasner et al. 1989). Cyanogen chloride was qualitatively detected during a 1975 survey of Cincinnati, Ohio drinking water (Kopfler et al. 1977). A 10-city survey that was conducted as part of the 1974 EPA National Organics Reconnaissance Survey revealed that cyanogen chloride was present in 8 of 10 drinking water supplies analyzed (no quantitative concentration values were provided) (Bedding et al. 1982). In a 1988 survey of 35 water utilities, the quarterly median cyanogen chloride concentrations in drinking water were 0.45–0.80 µg/L (Krasner et al. 1989).

No recent information could be found in the available literature on the levels of thiocyanate in groundwater, surface water, or drinking water. Thiocyanate is found at concentrations of 100–4,000 mg/L in coal and coke plant wastewaters (Ganczarczyk 1979; Jensen and Tuan 1993; Xiao et al. 2023) and 300–450 mg/L in mining (gold extraction) wastewaters (Boucabeille et al. 1994b).

5. POTENTIAL FOR HUMAN EXPOSURE

5.5.3 Sediment and Soil

Limited information was found in the available literature on concentrations of cyanides in soil or sediments at several hazardous waste sites. Cyanide concentrations were between 0.32 and 0.95 mg/kg near the Techatticup mining site in Nelson, Nevada (Sims and Francis 2008). In a review, Jaszczak et al. (2017) reported the following ranges of concentrations for various locations: soil near coking plant sites in France and Germany, 0.14–46.5 mg/L; soil near a Brazilian goldmine, 0.83–1.44 mg/kg; and soil near a Chinese goldmine, 70.55 mg/kg.

In general, the highly volatile gases hydrogen cyanide, cyanogen, and cyanogen chloride (see Table 4-2) would not be expected to be present in sediment or soil in any appreciable amounts. Also, degradation by microorganisms in soil can convert cyanide to carbon dioxide, ammonia, and other nitrogen compounds that will rapidly volatilize from soils (CEPA 1997).

Monitoring data on thiocyanate concentrations in soils are scarce. Concentrations of thiocyanate in soils amended with defatted seed meal of *Brassica napus L.* (rapeseed) were reported to be on the order of 6 µg/g (Brown et al. 1991).

5.5.4 Other Media

The primary cyanide source in food is cyanogenic glycosides. Plants containing cyanogenic glycosides can produce hydrogen cyanide by acid hydrolysis or by the action of the enzyme β -glucosidase (EPA 1980, 1981; Jones 1998; Seigler 1991). Hydrogen cyanide release can occur either during maceration, which activates the intracellular β -glucosidase, or in the gut by the action of β -glucosidase produced by microflora. The level of activity of β -glucosidase in the gut depends on the bacterial composition and the pH level (WHO 1992, 2004). There are approximately 60 known cyanogenic glycosides, which differ in their bioavailability (Seigler 1991). For example, cyanide production from the ingestion of seeds containing prunasin does not occur unless the seeds have been crushed. The potential toxicity of cyanogenic plants depends on their ability to release hydrogen cyanide during preparation or digestion at concentrations high enough to be of concern for human health (WHO 1992, 2004).

Over 2,650 plant species can produce hydrogen cyanide (Seigler 1991; Swain et al. 1992). These include edible plants such as almonds, pits from stone fruits (e.g., apricots, peaches, plums, cherries), sorghum, cassava, soybeans, spinach, lima beans, sweet potatoes, maize, millet, sugarcane, and bamboo shoots

5. POTENTIAL FOR HUMAN EXPOSURE

(EPA 1981). The cyanogenic glycoside content of a foodstuff is usually expressed as the amount of cyanide released by acid hydrolysis; glycoside concentrations are rarely reported (WHO 1992).

Cyanide levels measured in some foods are as follows: cereal grains and their products, 0.001–0.45 µg/g; soy protein products, 0.07–0.3 µg/g; and lima beans, 0.1–3 mg/g (EPA 1978; Honig et al. 1983). The cyanide equivalent of total cyanogenic content (i.e., cyanogenic glycosides, cyanohydrins, and hydrogen cyanide) of cassava root has been reported to range from 91 to 1,515 mg/kg hydrogen cyanide (86–1,458 µg/g CN⁻) dry weight (d/w) (O'Brien et al. 1992). Cassava is the major starchy food for more than 300 million people in many tropical countries of the world, and many cultivars are toxic (Seigler 1991). Effective processing can reduce the amount of total cyanogen in fresh cassava roots to significantly lower levels in foods ready for consumption (Mlingi et al. 1993; O'Brien et al. 1992). For example, while hydrogen cyanide is detected in nearly all (98.3%) samples of garri (a flour product of grated, pressed, and fermented cassava root pulp) from five agroecological zones in Nigeria, levels were much lower than in raw cassava root (0.056–2.463 mg/kg hydrogen cyanide; 0.054–2.364 µg/g CN⁻) (Olorunnado et al. 2024). A somewhat wider distribution of results was obtained in an older evaluation of commercial garri from three main garri-producing Nigerian communities (Aletor 1993). The mean total cyanide content (glucosidic plus non-glucosidic) of 38.8% of all samples (n=108) ranged from 0 to 10 mg/kg hydrogen cyanide (0–9.6 µg/g CN⁻), whereas 40.7, 12.9, and 7.4% of the samples had mean total cyanide contents of 10–20, 20–30, and 30–40 mg/kg hydrogen cyanide (9.6–19, 19–29, and 29–39 µg/g CN⁻), respectively. The mean cyanide content of domestic samples of “sweet” to “bitter” cassava food products in Cameroon was reported to range from 18.6 to 94.9 mg/kg hydrogen cyanide (17.9–91.4 µg/g CN⁻) d/w for a dried cassava flour, and from 0.0 to 0.9 mg/kg hydrogen cyanide (0.0–0.9 µg/g CN⁻) d/w for a cassava paste (O'Brien et al. 1992). Improper processing of cassava roots may result in maintenance of cyanogenic content of cassava food products at levels that are toxic (Mlingi et al. 1992, 1993; O'Brien et al. 1992). Cassava is a starch staple, but it is low in protein (Gomez et al. 1988). Low protein intake results in a decrease in available sulfur for conversion of cyanide to thiocyanate (Mlingi et al. 1993; Tylleskar et al. 1992). Hydrogen cyanide concentrations in sorghum leaves have been reported to range from approximately 200 to 1,300 ppm (192–1,250 µg/g CN⁻) wet weight (w/w), with higher concentrations observed in early growth stages and at lower levels of phosphorus fertilization (Chand et al. 1992).

In apricot pits, the cyanide concentration may vary from 8.9 to 217 mg/100 g (89–2,170 µg/g) w/w, depending on the type of cultivar, season, and geographic area (Lasch and El Shawa 1981). Swain et al. (1992) reported a mean cyanide concentration in black cherry (*Prunus serotina Ehrh.*) fruits somewhat >3 µmol/seed at maturity, which is equivalent to a mean cyanide content of 78 µg/seed; insufficient

5. POTENTIAL FOR HUMAN EXPOSURE

information was provided to allow conversion of these results to weight per weight (w:w) units. Voldrich and Kyzlink (1992) reported cyanide concentrations in canned unpitted fruits (peaches, apricots, plums, and cherries) of 0–4 mg/kg ($\mu\text{g/g}$) w/w, depending on the glycoside content of the raw fruits and the conditions of heat processing. The study authors noted that the observed cyanide levels were not negligible relative to an allowable daily intake (ADI) value for cyanide of 0.05 mg/kg body weight. An adult (70 kg body weight) could consume approximately 1 kg of canned fruits with a cyanide content of 4 mg/kg without exceeding this ADI value; however, a safe portion for a child (15 kg body weight) would be only about 180 g (12 mg/kg). The analysis of 233 samples of commercially available and homemade stone-fruit juices showed that pitted fruit juices had lower cyanide concentrations than unpitted or partially pitted fruit juices, indicating that the pits are the primary sources of cyanides in these juices (Stadelmann 1976). For example, the hydrogen cyanide content of a homemade mixed cherry juice from pitted fruits was 5.3 mg/L, compared to 23.5 mg/L in a cherry juice containing 100% crushed pits. This study also reported the following levels (median concentrations in mg/L) of hydrogen cyanide in commercial fruit juices: cherry, 4.6; apricot, 2.2; prune, 1.9; and peach, 2.9. Stadelmann (1976) recommended that the maximum hydrogen cyanide content allowed in fruit juices should be set at a level of 5 mg/L.

Cyanide can also be present in foodstuffs as residues from cyanide fumigation (EPA 1981). Human exposure to naturally occurring cyanide in foods in the United States is expected to be low compared to certain populations in the Third World that subsist on cassava and similar crops (EPA 1981).

Edible plants such as kale, cabbage, radishes, broccoli, brussels sprouts, cauliflower, collards, mustard greens, turnips, and kohlrabi contain glucosinolates and are hydrolyzed by the endogenous enzyme, myrosinase, to produce toxic products, including thiocyanate (Abukutsa et al. 1993; Bible and Chong 1975; Bible et al. 1980; Carlson et al. 1985, 1987; Olea and Parras 1992; Olea-Serano et al. 1988). Vegetables from the *Brassica* family (e.g., cabbages, kohlrabi, kale) contain high levels of thiocyanate ranging from 5 to 660 $\mu\text{g/g}$ w/w (Weuffen et al. 1984). Kale leaves have been reported to contain concentrations of potassium thiocyanate at harvest ranging from 447 to 5,067 ppm ($\mu\text{g/g}$) d/w (equivalent to thiocyanate concentrations of 267–3,035 $\mu\text{g/g}$ d/w) depending on the fertilizer nitrogen source (Abukutsa et al. 1993). Other commonly consumed vegetables (e.g., lettuce, spinach, radishes) have been found to contain thiocyanate at concentrations of ~0.1–5.0 $\mu\text{g/g}$ w/w, with concentrations usually <2.0 $\mu\text{g/g}$ w/w (Weuffen et al. 1984). Milk and other dairy products have been reported to contain thiocyanate at concentrations of 0.10–16.20 $\mu\text{g/g}$, whereas concentrations in meat products have been reported as 0.5–0.7 $\mu\text{g/g}$ (Weuffen et al. 1984; Yong et al. 2017).

5. POTENTIAL FOR HUMAN EXPOSURE

A 2018 study that looked at cyanide toxicity for frequently consumed smoothies and juices reported that the highest CN⁻ content was in drinks containing raw almond milk and fresh whole apple juice (Baker et al. 2018). Concentrations were detected as high as 341 µg/L in commercially available smoothies containing vegetables, raw flax seeds, almond milk, and fruits. Smoothies with vegetables, fruits, unpasteurized almond milk, and no flax seeds contained 41 µg/L, while similar smoothies containing pasteurized almond milk contained up to 9.6 µg/L.

Laetrile (amygdalin), a drug formerly used in clinical trials for the treatment of cancer (Khandekar and Edelman 1979); sodium nitroprusside, a drug used to reduce high blood pressure (Aitken et al. 1977; Vesey et al. 1976); and a series of commercially important, simple, aliphatic nitriles (e.g., acetonitrile, propionitrile, acrylonitrile, n-butyronitrile, maleonitrile, succinonitrile) (Willhite and Smith 1981) release cyanide upon metabolism. These drugs and industrial chemicals have been associated with human exposure to cyanide and have caused serious poisoning and, in some cases, death.

Reported levels of cyanide in tobacco smoke are quite variable. Cyanide levels in mainstream (inhaled) smoke from U.S. commercial cigarettes have been reported to range from 10 to 400 µg per cigarette, with the ratio of cyanide concentration in sidestream smoke to mainstream smoke ranging from 0.006 to 0.27 per cigarette (Chepiga et al. 2000; EPA 1981). In studies that included non-U.S. commercial cigarettes, hydrogen cyanide concentrations in mainstream and sidestream smoke were 280–550 and 53–111 µg/cigarette, respectively, have been reported; sidestream/mainstream ratios of hydrogen cyanide concentrations ranged from 0.06 to 0.50 (Baker and Proctor 1990; Guerin et al. 1987). In a 2017 review (Jaszczak et al. 2017), the levels of hydrogen cyanide in mainstream smoke were 6.6–184 µg per cigarette. In another study that looked at the levels of hydrogen cyanide in a wide range of cigarette and cigar products, a range of 17.56–1553 µg/stick was found (Mahernia et al. 2015).

5.6 GENERAL POPULATION EXPOSURE

The general population may be exposed to cyanide from inhaling air and ingesting food and drinking water contaminated with it. Since most of the cyanide in the air will be present as hydrogen cyanide (see Section 5.4.2), the primary inhalation exposure to cyanide will occur from hydrogen cyanide. The concentration of hydrogen cyanide in the air of non-urban areas is ≈160–166 ppt (see Section 5.5.1). Based on an atmospheric hydrogen cyanide concentration of 170 ppt (0.191 mg/m³) and an average daily

5. POTENTIAL FOR HUMAN EXPOSURE

inhalation volume of 20 m³, the inhalation exposure of the general U.S. non-urban, nonsmoking population to hydrogen cyanide is estimated to be 3.8 µg/day.

Vapor intrusion may be a potential source of hydrogen cyanide exposure, although indoor and ambient sources may also contribute to indoor air levels. The EPA (2016) includes hydrogen cyanide in its Vapor Intrusion Screening Levels (VISL) Calculator, indicating that it is sufficiently volatile and sufficiently toxic to be considered a concern for vapor intrusion from soil water and groundwater. Accordingly, ATSDR (2016) recommends that health assessors should evaluate potential health implications of vapor intrusion for hydrogen cyanide during site risk assessments. Tran et al. (2022) assessed risk of vapor intrusion of cyanide in villages near the largest gold mine in Thailand (Phichit's Gold Mine) due to several incidents of leakage or illegal discharge of cyanide-contaminated gold mine wastewater in Asia. The specific incident investigated was the “black water incident” of February 2015, in which the mining tailing storage facility leaked “black water” containing 2.13 mg/L cyanide into a nearby rice paddy, lotus pond, and creek. Speciation of the cyanide (11.30% free cyanide, 80.43% weak metal complex, and 8.26% strong acid dissociable) along with atmospheric modeling determined that up to 23 nearby villages were at elevated risk of acute health effects due to vapor intrusion from this and future incidents if seepages contain cyanide levels >0.65 mg/L.

Hydrogen cyanide in water is expected to rapidly volatilize; thus, there is potential for inhalation exposure during domestic water use activities, primarily showering and bathing. ATSDR’s three-compartment Shower and Household-Use Exposure (SHOWER) model predicts air concentrations in the shower stall, bathroom, and main house throughout the day by estimating the contribution from showering or bathing and the contribution from other water sources in the house, such as the dishwasher, clothes washer, and faucets (ATSDR 2022b). This information, along with human activity patterns, is used to calculate a daily time-weighted average (TWA) exposure concentration via inhalation exposure and from dermal uptake from skin contact. ATSDR’s SHOWER model is available by sending a request to showermodel@cdc.gov. Using a median value of 0.3 µg/L from the typical range for cyanide in treated water levels as discussed in Section 5.5.2 (based on WQP 2024) and a conservative representative outdoor air level of 0.33 µg/L as discussed in Section 5.5.1 (based on Jaszczak et al. 2017), reasonable maximum exposure (RME) levels were calculated for hydrogen cyanide (ATSDR 2022b). RME levels for different exposure groups are shown in Table 5-10.

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-10. Reasonable Maximum Exposure Daily Inhalation Concentration and Administered Dermal Dose of Hydrogen Cyanide for the Target Person

Exposure group	Inhalation ($\mu\text{g}/\text{m}^3$)	Dermal ($\mu\text{g}/\text{kg}/\text{day}$)
Birth-<1 year	NC	4.2×10^{-5}
1-<2 years	NC	3.8×10^{-5}
2-<6 years	NC	3.4×10^{-5}
6-<11 years	NC	2.8×10^{-5}
11-<16 years	NC	2.3×10^{-5}
16-<21 years	NC	2.1×10^{-5}
Adult	NC	2.0×10^{-5}
Pregnant and breastfeeding women	NC	2.0×10^{-5}

NC = not calculated

Source: ATSDR 2022b

Water quality data from the United States spanning 4 decades (1981–2023) indicates that 99% of water samples contained cyanide at concentrations <10 $\mu\text{g}/\text{L}$ (WQP 2024). Using the upper cut-off (10 $\mu\text{g}/\text{L}$) and assuming a daily water consumption of 2 L for a 70-kg adult, the daily intake of cyanide for the general population is estimated at <0.02 mg. EPA has established an MCL of 0.2 mg/L for cyanide in drinking water (EPA 2009; see Chapter 7), which is equivalent to a daily intake of 0.4 mg, based on a daily drinking water consumption rate of 2 L for a 70-kg adult (EPA 1991). In chlorinated drinking water, cyanide may be present as cyanogen chloride (see Section 5.4.2), which is less volatile than hydrogen cyanide.

Estimates of the cyanide concentration in the total diet of a U.S. adult were not located in the available literature. Therefore, no estimate of daily cyanide intake from food can be made. In the United States, human exposure to cyanide from foods in which it occurs naturally is expected to be low, but it is likely to exceed cyanide intake from inhalation of air and ingestion of drinking water (CEPA 1997; EPA 1981). EPA has established tolerances in various foods ranging from 25 to 250 ppm for hydrogen cyanide and from 5 to 25 ppm for calcium cyanide (EPA 1981). Poitras et al. (1988) estimated an overall allowable daily intake of 0.6 mg for cyanide, incorporating an uncertainty factor of 100–1,000 to ensure that the potential for an infant receiving a toxic dose of cyanide from breastmilk is quite low.

The primary route of exposure to thiocyanates for the general population appears to be from ingestion of foods in which thiocyanate occurs naturally (e.g., cabbage, kale, spinach, kohlrabi). Estimates of the thiocyanate concentration in the total diet of an adult in the United States were not located in the available

5. POTENTIAL FOR HUMAN EXPOSURE

literature; however, these would be expected to be quite low. Exposure to cyanide also is a source of thiocyanate exposure because thiocyanate is a major metabolite of cyanide in the human body.

Urinary thiocyanate levels are available from the National Health and Nutrition Examination Survey (NHANES) for 2011–2016. The geometric means and selected percentiles of urinary levels of cyanide for smokers and nonsmokers are shown in Tables 5-11 and 5-12, respectively; creatinine-corrected urinary levels are shown in Tables 5-13 and 5-14, respectively (CDC 2024).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Among the general population, subpopulations with the most likely potential for exposure to cyanide and thiocyanate include active and passive smokers (EPA 1981) and people who are exposed to house or other building fires (Andrews et al. 1989; Ballantyne 1987; Bolstad-Johnson et al. 2000). Other subpopulations with potentially high cyanide or thiocyanate exposures are residents who live near industrial sites releasing cyanides or thiocyanates into the environment, residents who live near cyanide- or thiocyanate-containing hazardous waste sites, and people who consume foods high in cyanogenic glycosides. The fetuses of pregnant women who smoke or who are exposed to high levels of environmental smoke and the children of smokers may be subjected to potentially high exposures of cyanide and thiocyanate (Bottoms et al. 1982; EPA 1992; Hauth et al. 1984).

NHANES data from 2011–2016 (Tables 5-11 through 5-14) show elevated urinary cyanide and thiocyanate concentrations in smokers, compared to nonsmokers (CDC 2024). The results of several additional studies that have shown similar elevations in cyanide or thiocyanate concentrations in body fluids of smokers, compared to nonsmokers; these studies are summarized in Table 5-15. In general, these results indicate that serum cyanide levels (Cardeal et al. 1993; Symington et al. 1987; Tsuge et al. 2000) and plasma, serum, and saliva thiocyanate levels (Banerjee and Muthu 1994; Jarvis 1989; Maliszewski and Bass 1955; Pré and Vassy 1992, 1993; Tsuge et al. 2000; Waage et al. 1992; Yamanaka et al. 1991) could distinguish smokers from nonsmokers and/or light smokers. Pré and Vassy (1992) found that plasma thiocyanate was an indicator of smoking status that was not sensitive to light or passive smoking. However, inhaling smokers were easily distinguished from noninhaling smokers. The study authors concluded that a plasma thiocyanate concentration <20 µmol/L (1,200 µg/L) indicated that passive smoking was very unlikely, whereas concentrations >80–85 µmol/L (4,600–4,900 µg/L) were a reliable indication of an active inhalation of smoke. Yamanaka et al. (1991) found a correlation between

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-11. Urinary Thiocyanate Concentrations (mg/L) in the Cigarette Smoking^a U.S. General Population

Survey years	Geometric mean (95% confidence interval) ^b	Percentiles (95% confidence interval) ^b				Sample size
		50th	75th	90th	95th	
Total						
2011–2012	4.10 (3.58–4.69)	4.60 (3.98–5.37)	7.16 (6.43–8.09)	11.2 (9.43–12.7)	14.6 (12.7–16.2)	869
2013–2014	3.93 (3.56–4.33)	4.48 (3.93–4.78)	7.45 (6.70–8.23)	12.5 (10.2–14.0)	15.2 (13.9–17.7)	944
2015–2016	3.88 (3.47–4.33)	4.65 (3.91–5.51)	8.28 (7.72–8.57)	11.8 (11.1–13.0)	15.0 (13.7–16.5)	824
Age group						
20–49 years						
2011–2012	4.18 (3.72–4.69)	4.67 (4.15–5.05)	7.38 (6.43–8.20)	11.7 (10.2–13.3)	15.9 (12.7–17.8)	518
18–49 years						
2013–2014	3.99 (3.46–4.61)	4.72 (3.90–5.32)	7.90 (6.96–8.89)	13.5 (10.8–14.5)	16.0 (14.1–18.0)	575
2015–2016	3.52 (2.96–4.18)	4.16 (3.53–5.07)	8.33 (7.10–9.77)	12.9 (11.3–14.5)	16.3 (14.3–19.8)	448
≥50 years						
2011–2012	3.98 (3.24–4.90)	4.38 (3.37–5.94)	6.90 (5.48–8.14)	9.94 (7.67–13.5)	12.8 (9.50–15.3)	351
2013–2014	3.79 (3.40–4.23)	3.87 (3.41–4.63)	6.53 (5.45–7.58)	9.98 (9.02–12.6)	14.4 (11.5–18.3)	369
2015–2016	4.51 (3.73–5.45)	5.36 (3.91–6.41)	7.88 (6.89–9.02)	10.5 (9.39–12.1)	12.8 (11.1–15.5)	376
Gender						
Males						
2011–2012	4.03 (3.26–4.98)	4.51 (3.30–6.14)	7.23 (6.43–8.59)	11.1 (8.99–13.4)	14.5 (11.8–17.8)	525
2013–2014	3.81 (3.31–4.39)	4.63 (3.73–5.19)	7.59 (6.60–8.92)	13.5 (10.7–14.5)	15.6 (14.1–18.5)	508
2015–2016	3.64 (2.99–4.44)	4.22 (3.40–5.65)	8.64 (7.69–9.70)	12.4 (11.1–14.8)	15.5 (13.7–19.5)	485
Females						
2011–2012	4.19 (3.81–4.61)	4.71 (4.31–5.37)	6.83 (6.12–7.95)	11.3 (8.53–13.1)	15.3 (11.9–18.2)	344
2013–2014	4.05 (3.61–4.54)	4.30 (3.88–4.78)	7.15 (6.16–8.24)	11.3 (9.40–14.1)	14.5 (11.3–17.7)	436
2015–2016	4.19 (3.73–4.70)	5.03 (4.06–5.92)	7.93 (7.35–8.33)	10.8 (9.58–12.7)	13.9 (11.7–18.8)	339

^aCigarette smokers were defined by an affirmative response to the question, 'Have you smoked at least 100 cigarettes in your life?' and confirmation that they smoke either every day or some days.

^bLimits of detection for survey years 2011–2012, 2013–2014, and 2015–2016 were 0.020, 0.020, and 0.020 mg/L, respectively.

Source: CDC 2024

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-12. Urinary Thiocyanate Concentrations (mg/L) in the Nonsmoking^a U.S. General Population

Survey years	Geometric mean (95% confidence interval) ^b	Percentiles (95% confidence interval) ^b				Sample size
		50th	75th	90th	95th	
Total						
2011–2012	0.795 (0.737–0.858)	0.875 (0.819–0.929)	1.56 (1.41–1.74)	2.54 (2.23–2.92)	3.23 (2.97–3.57)	1,319
2013–2014	0.791 (0.745–0.841)	0.799 (0.737–0.861)	1.48 (1.37–1.55)	2.55 (2.31–2.89)	3.67 (2.96–4.47)	1,476
2015–2016	0.817 (0.740–0.901)	0.875 (0.762–0.979)	1.57 (1.39–1.81)	2.69 (2.48–3.12)	3.78 (3.13–4.54)	1,455
Age group						
20–49 years						
2011–2012	0.855 (0.777–0.940)	0.927 (0.854–1.00)	1.71 (1.50–1.92)	2.67 (2.29–3.17)	3.43 (3.01–4.36)	659
18–49 years						
2013–2014	0.838 (0.774–0.907)	0.862 (0.766–0.988)	1.54 (1.43–1.73)	2.54 (2.31–2.96)	3.75 (2.96–5.03)	774
2015–2016	0.894 (0.816–0.981)	0.904 (0.821–1.02)	1.74 (1.40–1.96)	3.02 (2.30–3.72)	3.92 (3.16–4.66)	741
≥50 years						
2011–2012	0.736 (0.666–0.814)	0.833 (0.726–0.897)	1.44 (1.21–1.68)	2.39 (1.94–2.90)	2.92 (2.39–3.86)	660
2013–2014	0.742 (0.668–0.824)	0.751 (0.668–0.843)	1.36 (1.19–1.57)	2.66 (1.96–3.26)	3.67 (2.70–4.81)	702
2015–2016	0.739 (0.630–0.868)	0.814 (0.687–1.01)	1.47 (1.23–1.76)	2.59 (2.18–3.03)	3.29 (2.60–4.28)	714
Gender						
Males						
2011–2012	0.968 (0.865–1.08)	1.01 (0.913–1.20)	1.90 (1.57–2.20)	2.79 (2.31–3.25)	3.43 (2.94–4.10)	628
2013–2014	0.938 (0.853–1.03)	0.911 (0.830–1.05)	1.79 (1.55–2.07)	2.96 (2.44–3.81)	4.33 (3.10–5.93)	661
2015–2016	1.00 (0.873–1.16)	1.06 (0.923–1.23)	1.86 (1.64–2.23)	3.25 (2.62–4.28)	4.58 (3.54–6.37)	658
Females						
2011–2012	0.681 (0.600–0.773)	0.727 (0.603–0.843)	1.36 (1.21–1.50)	2.27 (1.97–2.54)	3.17 (2.52–3.32)	691
2013–2014	0.687 (0.634–0.744)	0.694 (0.621–0.779)	1.29 (1.14–1.39)	2.20 (1.91–2.36)	3.10 (2.67–3.75)	815
2015–2016	0.690 (0.624–0.763)	0.723 (0.624–0.798)	1.31 (1.12–1.52)	2.35 (2.00–2.64)	3.02 (2.48–3.84)	797

^aCigarette nonsmokers who used other tobacco products were excluded.^bLimits of detection for Survey years 2011–2012, 2013–2014, and 2015–2016 were 0.020, 0.020, and 0.020 mg/L, respectively.

Source: CDC 2024

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-13. Urinary Thiocyanate Concentrations (Creatinine Corrected) (µg/g Creatinine) in the Cigarette Smoking^a U.S. General Population

Survey years	Geometric mean (95% confidence interval) ^b	Percentiles (95% confidence interval) ^b				Sample size
		50th	75th	90th	95th	
Total						
2011–2012	4.53 (4.02–5.10)	5.04 (4.38–5.47)	8.28 (7.42–10.0)	14.4 (11.6–15.7)	16.7 (15.3–18.9)	869
2013–2014	3.99 (3.57–4.47)	4.37 (3.99–5.00)	7.81 (7.12–8.51)	11.9 (10.4–14.3)	15.6 (13.5–18.6)	944
2015–2016	3.91 (3.51–4.36)	4.41 (3.74–5.21)	7.88 (6.97–8.75)	11.8 (10.8–12.8)	15.4 (13.4–16.4)	824
Age group						
20–49 years						
2011–2012	4.35 (3.87–4.89)	4.84 (3.82–5.47)	7.98 (7.54–8.91)	14.0 (11.1–16.1)	16.7 (14.2–19.9)	518
18–49 years						
2013–2014	3.69 (3.25–4.19)	4.17 (3.75–4.68)	7.40 (6.33–8.43)	11.7 (10.4–13.8)	14.4 (12.9–15.9)	575
2015–2016	3.30 (2.80–3.90)	3.96 (2.97–4.83)	6.99 (5.55–8.68)	10.4 (8.86–11.7)	11.8 (10.6–15.1)	448
≥50 years						
2011–2012	4.81 (4.06–5.71)	5.28 (4.43–6.84)	8.84 (7.11–12.1)	15.3 (10.5–17.2)	16.6 (15.3–18.3)	351
2013–2014	4.71 (4.16–5.34)	4.68 (4.42–5.62)	8.12 (7.37–9.45)	12.9 (10.3–18.4)	18.6 (11.0–22.8)	369
2015–2016	5.05 (4.28–5.96)	5.70 (4.25–6.77)	8.63 (7.78–11.0)	14.8 (11.5–16.2)	17.0 (14.8–24.8)	376
Gender						
Males						
2011–2012	3.81 (3.28–4.43)	4.20 (3.64–5.06)	7.30 (6.54–7.77)	11.1 (9.41–12.5)	14.3 (12.3–15.6)	525
2013–2014	3.38 (2.96–3.86)	4.14 (3.13–4.49)	7.12 (6.14–7.87)	11.0 (9.50–11.7)	13.2 (11.7–14.9)	508
2015–2016	3.17 (2.70–3.72)	3.34 (2.52–4.40)	6.85 (5.39–7.42)	10.2 (8.75–10.9)	12.2 (10.8–16.0)	485
Females						
2011–2012	5.62 (4.64–6.81)	5.82 (4.69–8.05)	11.1 (8.53–14.6)	16.7 (14.0–18.9)	19.2 (16.7–24.0)	344
2013–2014	4.73 (4.12–5.42)	4.87 (4.08–5.92)	8.19 (7.52–9.75)	13.8 (10.7–17.1)	17.9 (14.2–21.2)	436
2015–2016	5.03 (4.39–5.76)	5.86 (5.14–6.61)	8.83 (8.26–10.6)	13.9 (11.8–15.4)	15.8 (14.8–17.8)	339

^aCigarette smokers were defined by an affirmative response to the question, 'Have you smoked at least 100 cigarettes in your life?' and confirmation that they smoke either every day or some days.

^bLimits of detection for Survey years 2011–2012, 2013–2014, and 2015–2016 were 0.020, 0.020, and 0.020 mg/L, respectively.

Source: CDC 2024

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-14. Urinary Thiocyanate Concentrations (Creatinine Corrected) ($\mu\text{g/g}$ Creatinine) in the Nonsmoking^a U.S. General Population

Survey years	Geometric mean (95% confidence interval) ^b	Percentiles (95% confidence interval) ^b				Sample size
		50th	75th	90th	95th	
Total						
2011–2012	0.933 (0.881–0.988)	0.976 (0.905–1.10)	1.69 (1.54–1.84)	2.70 (2.34–2.99)	3.29 (3.02–3.89)	1,318
2013–2014	0.948 (0.882–1.02)	0.994 (0.908–1.06)	1.68 (1.54–1.80)	2.71 (2.28–3.00)	3.74 (3.13–4.47)	1,475
2015–2016	0.922 (0.844–1.01)	0.953 (0.874–1.08)	1.74 (1.56–1.87)	2.68 (2.40–2.88)	3.60 (3.11–4.10)	1,453
Age group						
20–49 years						
2011–2012	0.938 (0.864–1.02)	1.01 (0.902–1.10)	1.67 (1.46–1.84)	2.51 (2.18–2.91)	3.02 (2.91–3.18)	658
18–49 years						
2013–2014	0.922 (0.843–1.01)	0.950 (0.860–1.04)	1.52 (1.37–1.66)	2.33 (2.09–2.57)	3.37 (2.60–4.40)	774
2015–2016	0.934 (0.865–1.01)	0.898 (0.815–1.04)	1.66 (1.50–1.81)	2.54 (2.23–3.15)	3.74 (3.13–4.59)	739
≥50 years						
2011–2012	0.927 (0.852–1.01)	0.965 (0.830–1.18)	1.72 (1.46–1.99)	2.91 (2.16–3.37)	3.76 (3.16–4.33)	660
2013–2014	0.979 (0.880–1.09)	1.05 (0.890–1.24)	1.85 (1.55–2.08)	2.92 (2.41–3.56)	4.13 (3.14–5.08)	701
2015–2016	0.910 (0.780–1.06)	1.03 (0.881–1.22)	1.85 (1.47–2.14)	2.68 (2.22–3.14)	3.60 (2.78–4.39)	714
Gender						
Males						
2011–2012	0.865 (0.782–0.956)	0.941 (0.743–1.09)	1.56 (1.28–1.87)	2.66 (2.09–2.96)	3.37 (2.67–4.05)	627
2013–2014	0.912 (0.832–0.999)	0.983 (0.854–1.12)	1.62 (1.47–1.82)	2.75 (2.17–3.19)	4.13 (2.88–5.08)	660
2015–2016	0.923 (0.812–1.05)	0.944 (0.814–1.18)	1.77 (1.50–1.98)	2.81 (2.30–3.27)	3.87 (2.89–5.02)	658
Females						
2011–2012	0.990 (0.910–1.08)	1.05 (0.936–1.17)	1.75 (1.59–1.91)	2.86 (2.41–3.03)	3.29 (2.97–3.96)	691
2013–2014	0.980 (0.910–1.05)	1.01 (0.923–1.06)	1.71 (1.55–1.81)	2.69 (2.26–3.13)	3.53 (2.94–4.15)	815
2015–2016	0.921 (0.836–1.02)	0.955 (0.874–1.05)	1.73 (1.56–1.86)	2.52 (2.38–2.88)	3.58 (2.88–4.14)	795

^aCigarette nonsmokers who used other tobacco products were excluded.

^bLimits of detection for Survey years 2011–2012, 2013–2014, and 2015–2016 were 0.020, 0.020, and 0.020 mg/L, respectively.

Source: CDC 2024

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-15. Cyanide and Thiocyanate Concentrations ($\mu\text{g/mL}$)^a in Smokers and Nonsmokers

Compound	Plasma/blood		Serum		Saliva		Urine		Reference
	Smoker	Nonsmoker	Smoker	Nonsmoker	Smoker	Nonsmoker	Smoker	Nonsmoker	
Cyanide			2.11 (1.42–3.67)	0.78 (0.44–1.15)					Cardeal et al. 1993 ^b
			6.8 (1.3–19.4)	2.9 (0.0–11.7)					Symington et al. 1987 ^{b,c}
	0.27 (0.14– 0.41) ^d	0.17 (0.11–0.25) ^d			0.66 (0.13–2.07) ^d	0.38 (0.05–1.20) ^d			Tsuge et al. 2000
Thiocyanate			232 (10)	92 (9)					Banerjee and Muthu 1994 ^e
	7.1	2.9			142	76	9.0	5.8	Jarvis 1989 ^f
	7.1 (6.2–8.6)	2.0 (1.2–2.8)			75.7 (48.4–112.2)	20.3 (9.71–28.7)	12.3 (7.8–17.2)	2.1 (1.1–3.9)	Maliszewski and Bass 1955 ^b
	8.7 ^g (4.4–21.5)	1.8 ^h (0.5–4.4)							Pré and Vassy 1992 ^e
	3.3 ⁱ (1.0–4.6)								
			6.6 (1.5)	1.2 (0.3)					Pré and Vassy 1993 ^e
	111.2 (1.7–290) ^d	33.5 (6.3–94) ^d			1,655 (270–2,940) ^d	542 (13–1,630) ^d			Tsuge et al. 2000

5. POTENTIAL FOR HUMAN EXPOSURE

Table 5-15. Cyanide and Thiocyanate Concentrations ($\mu\text{g/mL}$)^a in Smokers and Nonsmokers

Compound	Plasma/blood		Serum		Saliva		Urine		Reference
	Smoker	Nonsmoker	Smoker	Nonsmoker	Smoker	Nonsmoker	Smoker	Nonsmoker	
	(<0.05 – 0.35)	(<0.05 – 0.08)							
2.1	3.7				88	33	18	19	Waage et al. 1992 ^{e,j} Yamanaka et al. 1991 ^{j,k}

^aValues are means; values in parentheses are ranges or standard deviations.

^bNo statistics reported.

^cAs cited in Cardeal et al. (1993).

^dValues are expressed as μM ; values in parentheses are ranges.

^eResults significantly different.

^fResults not significantly different.

^gInhaling smokers.

^hNonsmokers including passive smokers.

ⁱNoninhaling smokers.

^jValues estimated from graphical presentation of data.

^kAll results, except urine, are significantly different.

5. POTENTIAL FOR HUMAN EXPOSURE

the number of cigarettes smoked per day and the thiocyanate levels in plasma and saliva; however, in apparent contrast to results obtained by Maliszewski and Bass (1955), thiocyanate concentrations in urine of smokers and nonsmokers were not found to be significantly different.

No data were found related to the levels of cyanide or thiocyanate exposure in cassava eaters in the United States. However, elevated levels of thiocyanate in body fluids resulting from consumption of cyanide-containing foods have been reported in populations from tropical regions that may consume large quantities of improperly processed cyanogenic plants such as cassava (WHO 2004). Among four populations in Africa known to be exposed to high levels of dietary cyanide because of incomplete processing of cassava during drought periods, urinary thiocyanate concentrations (mean \pm standard error) ranged from 350 ± 39 to $1,120\pm75$ $\mu\text{mol/L}$ (20 ± 2 – 65 ± 4 mg/L), compared to urinary thiocyanate levels in the normal population of <100 $\mu\text{mol/L}$ (5.8 $\mu\text{g/L}$) (Mlingi et al. 1992, 1993; Tylleskar et al. 1992). The mean plasma thiocyanate concentration in one of these populations was 335 ± 12 $\mu\text{mol/L}$ (19 ± 1 $\mu\text{g/L}$), compared to 28 ± 4 $\mu\text{mol/L}$ (1.6 ± 0.2 $\mu\text{g/L}$) in a control population (Mlingi et al. 1992). Elevated mean serum thiocyanate concentrations (11 ± 3 $\mu\text{g/L}$ compared to reference values of 0.5 – 4 $\mu\text{g/L}$) were observed in only one of two populations in which this biomarker was measured (Tylleskar et al. 1992, 1994). There was no apparent explanation for this difference.

The dietary cyanide intake of Tukanoan Indians in northwest Amazonia who rely heavily on high (>70% of all foods) cyanide-containing varieties of cassava was estimated to be >20 mg/day (Dufour 1988). High serum thiocyanate concentrations (>180 $\mu\text{mol/L}$) were also reported in this population. Yet, Dufour (1988) did not find physical disorders in Tukanoan Indians attributable to high cassava diets, in contrast to observations related to cassava-consuming populations in Africa. One reason that has been suggested is that the cassava processing techniques of the Tukanoans are very sophisticated and very effective in reducing the cyanide concentration in the crop. Indeed, it has been shown in several studies of cassava processing techniques used in Africa that the level of hydrogen cyanide can be effectively and reliably reduced by allowing sufficient time for the hydrolysis of cyanogenic glucosides and evaporation of hydrogen cyanide (Ojo and Deane 2002; Onabolu et al. 2002). Another reason that may account for the observed differences in toxicity among different populations is that the variety of cassava may differ between geographical areas (Panghal et al. 2019). When outbreaks of acute cyanide intoxications from incomplete processing of cassava occur in African populations, highly elevated cyanide levels were observed in combination with chronic dietary protein malnutrition (WHO 2004). This occurred when, due to a food shortage, the lengthy sun drying normally used to remove cyanogenic glucosides was

5. POTENTIAL FOR HUMAN EXPOSURE

replaced by repeated pounding and drying to obtain flour for consumption in 1 day (Mlingi et al. 1992, 1993; Tylleskar et al. 1992).

Workers involved in electroplating, metallurgy, pesticide application, firefighting, gas works operations, tanning, blacksmithing, metal cleaning, photoengraving, photography, cyanotype printing, the manufacture of steel, cyanides, adiponitrile and other nitriles, methyl methacrylate, cyanuric acid, dyes, pharmaceuticals, or chelating agents have the potential to be occupationally exposed to higher concentrations of cyanide than the general population (EPA 1981; NIOSH 1989). Workers in the following industries may also be exposed to higher concentrations of thiocyanate than the general population: manufacture of electronic computing equipment, research and development laboratories, newspaper and other commercial printing, general medical or surgical hospitals, production of adhesives and sealants, pesticide application, building and furniture construction, and handling, treatment, or disposal of thiocyanate-containing wastes from industrial processes (Brown and Morra 1993; NIOSH 1989; WHO 2004). Two additional groups of people who may be at greater risk for cyanide exposure are those who are exposed to cyanide but are unable to smell the chemical (EPA 1987) and patients with motor neuron disease (Kato et al. 1985).

Occupational exposures to cyanide are expected to occur primarily through inhalation and, less frequently, through skin absorption. Preliminary data from the NOES conducted by the National Institute for Occupational Safety and Health (NIOSH) from 1980 to 1983 estimated that the number of workers potentially exposed to cyanide compounds in the United States in 1981–1983 are as follows (NIOSH 1989): cyanide, 367; hydrogen cyanide, 4,005; sodium cyanide, 66,493; potassium cyanide, 64,244; potassium silver cyanide, 3,215; calcium cyanide, 3,606; copper (I) cyanide, 22,339; ammonium thiocyanate, 90,599; and cyanogen chloride, 1,393. Thiocyanate and cyanogen were not included in the NOES (NIOSH 1989). These numbers do not include workers potentially exposed to tradename compounds that contain cyanides or thiocyanates. Workers in various occupations may be exposed to cyanide compounds. People possibly exposed to cyanide include workers involved in electroplating, metallurgy, cyanotype printing, pesticide application, firefighting, steel manufacturing, and gas works operations; workers involved in the manufacture of cyanides, adiponitrile and other simple, aliphatic nitriles, methyl methacrylate, cyanuric acid, dyes, pharmaceuticals, or chelating agents; and people who work in tanneries, blacksmithing, metal cleaning, and photoengraving or photography industries (EPA 1981; Lucas 1992; WHO 2004; Willhite and Smith 1981). Workers in the oil shale retorting industry may be exposed to cyanide because the offgas from the retorting process contains hydrogen cyanide (see Section 5.3.1). There is a reported case of the fatal poisoning of three trawler crew members as they

5. POTENTIAL FOR HUMAN EXPOSURE

entered a refrigerated compartment containing spoiled fish in which cyanide, in addition to methane and hydrogen sulfide, have been implicated in their deaths (Cherian and Richmond 2000). Medical and emergency personnel (e.g., police and firefighters) who may be involved in resuscitation efforts or removal of gastric contents of postmortem victims of cyanide poisoning are potentially exposed to higher levels of cyanide (Andrews et al. 1989; Bolstad-Johnson et al. 2000; Nolte and Dasgupta 1996). Workers involved in large-scale processing of cassava have been shown to have thiocyanate levels in urine that are 2.2–2.6 times the levels found in individuals who regularly consume cassava products (Okafor et al. 2002). The increased thiocyanate levels in cassava processors are due to inhalation of hydrogen cyanide that is discharged to air during the processing of cassava. The manufacture of industrial inorganic chemicals may be a significant potential source of occupational exposure to cyanogen chloride (NIOSH 1989). Potential sources of occupational exposure to ammonium thiocyanate include the manufacture of electronic computing equipment, research and development laboratories, newspaper and other commercial printing, general medical and surgical hospitals, production of adhesives and sealants, and the construction and furniture industries (NIOSH 1989).

In a survey of the plating facility of a national airline conducted by NIOSH in December 1981, the concentrations of hydrogen cyanide in three work areas were 0.001–0.004 mg/m³ (0.0009–0.004 ppm) (NIOSH 1982). The cyanide concentrations in four work areas in a plating facility of an electrical and electronic company in Waynesboro, Virginia, ranged from 0.07 mg/m³ (0.07 ppm hydrogen cyanide) in a salt pot room to 4.3 mg/m³ (4.0 ppm hydrogen cyanide) beside a stripping tank (NIOSH 1976). Similarly, the concentration of cyanide in the breathing zone air of workers in a plating facility in Galion, Ohio, was 1.7 mg/m³ (1.6 ppm hydrogen cyanide) (NIOSH 1978). In a NIOSH survey of a university art department foundry, hydrogen cyanide was detected in the smoke produced during pouring and knockout of castings at a concentration of approximately 4 ppm; hydrogen cyanide was not detected in personal breathing zone samples taken during knockout of castings (Lucas and Salisbury 1992). These levels are all below the NIOSH short-term exposure limit of 4.7 ppm (NIOSH 1992).