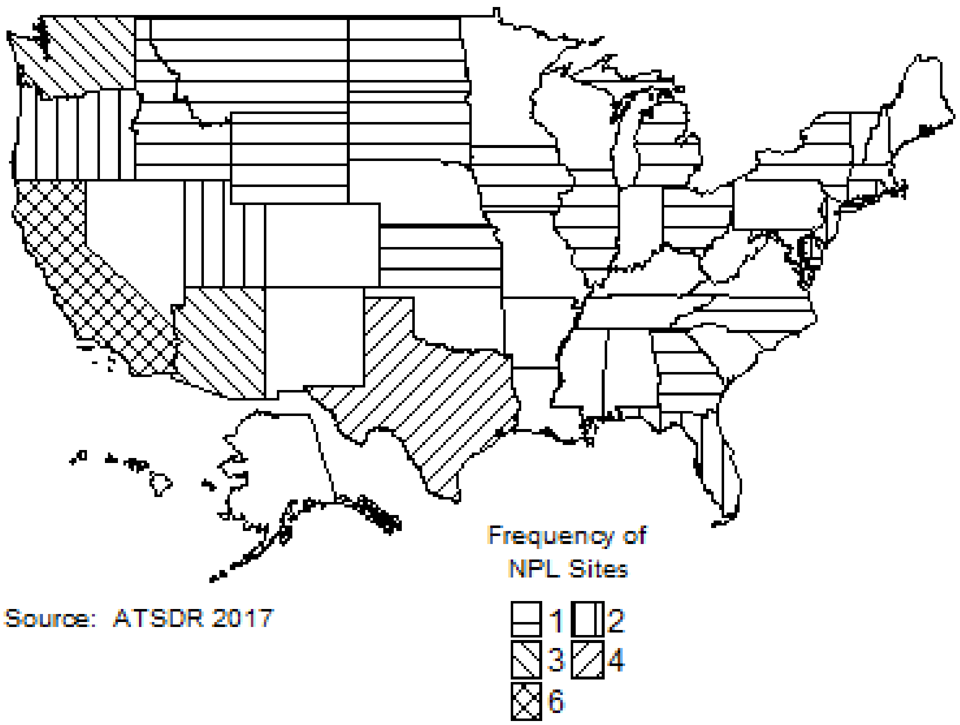
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Silica has been identified in at least 37 of the 1,854 hazardous waste sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (ATSDR 2017). However, the number of sites in which silica 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 Silica Contamination



Source: ATSDR 2017

Crystalline Silica

- c-Silica is ubiquitous and widespread in the environment, primarily in the form of quartz. Other predominant forms include cristobalite and tridymite.
- Sand, gravel, and quartz crystal are the predominant commercial product categories for c-silica.
- c-Silica enters environmental media naturally through the weathering of rocks and minerals and anthropogenic releases of c-silica in the form of air emissions (e.g., industrial quarrying and mining, metallurgic manufacturing, power plant emissions) or use in water filtration (quartz sand).

- c-Silica undergoes atmospheric transport as a fractional component of particulate emissions, is virtually insoluble in water and generally settles into sediment, and remains unchanged in soil.
- c-Silica is present in air and water; therefore, the general population will be exposed to c-silica by inhalation of ambient air and ingestion of water.
- Inhalation exposure is the most important route of exposure to c-silica compounds due to the development of adverse effects from inhaled c-silica in occupational settings.
- Individuals with potentially high exposures include workers with occupational exposure to c-silica, which occurs during the mining and processing of metals, nonmetals, and coal, and in many other industries.

Amorphous Silica

- a-Silica exists in natural forms that often contain various amounts of c-silica (diatomite, calcined, flux calcined, biogenic silica fibers, opal, vitreous silica) and in synthetic forms that are not contaminated with c-silica (pyrogenic, precipitated, gel, colloidal). Vitreous silica can also be intentionally produced, or may occur with a-silica fume as a by-product during certain industrial processes.
- a-Silica is used in a wide variety of industrial processes and consumer products (e.g., filtration systems, desiccants/absorbants, fillers, thickeners, pesticides, food additives, food wrappings, pharmaceuticals, cleaning products, cosmetic and personal hygiene products).
- Natural a-silica enters environmental media naturally primarily through biogenic sources (e.g., diatoms).
- Both natural and synthetic a-silica enter environmental media through anthropogenic releases of silica in the form of air emissions (e.g., industrial quarrying and mining, metallurgic manufacturing, power plant emissions), use in water filtration (diatomaceous earth), industrial waste waters (synthetic a-silica), or use as a pesticide (diatomaceous earth, a-silica gel).
- a-Silica undergoes atmospheric transport as a fractional component of particulate emissions, is poorly soluble in water (although does dissolve to some degree) and mainly settles into sediment, and remains unchanged in soil. Aquatic and terrestrial plants uptake bioavailable forms of a-silica from sediment and soil, respectively.
- a-Silica is present in air and water; therefore, the general population will be exposed to a-silica by inhalation of ambient air and ingestion of water.
- Synthetic a-silica also is used as an additive in food and in food packaging; therefore, food is expected to be a source of exposure to a-silica for most people.

- Inhalation exposure is expected to be the most important route of exposure to a-silica compounds due to the development of adverse effects in animals from inhaled a-silica.
- Individuals with potentially high exposures include individuals with occupational exposure to a-silica, which may occur during the mining and processing of diatomaceous earth, metallurgic manufacturing, use or manufacture of synthetic a-silicas, and sugarcane and rice farming.

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

No information is available in the TRI database on facilities that manufacture or process silica because this chemical is not required to be reported under Section 313 of the Emergency Planning and Community Right-to-Know Act (Title III of the Superfund Amendments and Reauthorization Act of 1986) (EPA 2005).

Crystalline Silica. c-Silica exists in the natural environment (OSHA 2013c). Sand, gravel, and quartz crystals are the predominant commercial product categories for c-silica (IARC 2012). c-Silica is a common component of igneous rocks such as granite, rhyolite, quartz diorite, quartz monzonite, and andesite. Naturally occurring c-silica is mined from the earth’s crust (USGS 1992). Typically, c-silica is mined using open pit or dredging methods with standard mining equipment (USGS 2014b). The major component of sand and gravel is quartz. The quartz content of crushed stone varies from region to region.

The U.S. Geological Survey (USGS 2015) reported sand and gravel in two mineral commodity summaries, industrial sand and gravel or commercial sand and gravel. An estimated 139 million metric tons of silica, in the form of industrial sand and gravel, were produced throughout the world in 2012 (USGS 2014b). The United States (50.7 million metric tons), Italy (16.4 million metric tons), Germany (7.5 million metric tons), Turkey (7 million metric tons), France (6.3 million metric tons), Australia (5.3 million metric tons), Spain (5 million metric tons), the United Kingdom (3.8 million metric tons), and Japan (3.2 million metric tons) were the highest producing countries in 2012. The USGS performed a voluntary survey in 2012 of U.S. industrial sand and gravel producers from 77 operations, which represented 75% of the U.S. total production (combined). The survey data indicated that the Midwest produced over half (56%) of the 50.7 metric tons of industrial sand and gravel produced in the United States, followed by the South at 36%, the West at 5%, and the Northeast at 3% (USGS 2014b). Demand for hydraulic fracturing sand has resulted in increased industrial sand and gravel production capacity in the United States through ongoing permitting and opening of new mines (USGS 2015).

In 2012, the United States produced 812 million metric tons of construction sand and gravel (USGS 2014c). Construction sand and gravel were produced by 4,100 companies and government agencies in the United States (USGS 2015). Texas, California, Minnesota, Washington, Michigan, Colorado, Arizona, North Dakota, Wisconsin, and Ohio accounted for about 55% of total U.S. output.

Quartz crystal for electronics is predominantly from cultured, not natural, crystal. Synthetic quartz crystals are grown in specific shapes and sizes in heavy-duty autoclaves at 1,500–20,000 pounds/inch^2 and 250–450°C (USGS 1992). No companies in the United States reported production of cultured quartz crystal in a 2012 USGS voluntary survey (USGS 2014b). Cultured quartz crystal is produced primarily in Asia.

Quartz has two forms, α-quartz and β-quartz. The thermodynamically stable form of quartz under ambient conditions is α-quartz; β-quartz forms at temperatures >573°C (USGS 1992). Quartz has a range of physical forms with different sizes, shapes, surface area, roughness, and sorption capacity. Natural quartz is collected from ore through a beneficiation process where raw material is milled and ground into particles and separated into desired mineral and waste. Grinding of sand or gravel is sometimes required to achieve a desired silica material; these processes increase the levels of dust containing respirable c-silica (NTP 2014). Idiomorphic quartz, lump quartz, quartz pebbles, granular quartz, quartz sand, quartz powder, and quartz rock are quartz raw material forms (Florke et al. 2008). Silica flour is an extremely fine-grade silica sand product. Tripoli (CASRN 1317-95-9) is a form of microcrystalline quartz with an extremely small particle size (NIOSH 2011).

Cristobalite is a form of c-silica formed at temperatures >1,470°C (OSHA 2013c). Cristobalite may be formed from quartz during the pouring of metal in foundries where quartz is used to make molds and cores (IARC 1997). Tridymite is a form of c-silica formed at temperatures >870°C (OSHA 2013c). Both cristobalite and tridymite are found in volcanic rocks and glass (Mossman and Glenn 2013).

Flint, chalcedony, agate, chert, and novaculit are cryptocrystalline silica. Cryptocrystalline silica is silica with submicrometer crystals formed by geological crystallization or compaction of a-silica (IARC 1997; USGS 1992). Forms of c-silica are gemstones (USGS 2014a, 2015). The estimated values in 2012 of U.S. natural quartz gemstone production were $383,000 and $261,000 for macrocrystalline and cryptocrystalline quartz, respectively (quantity in mass not reported). The macrocrystalline quartz gemstones are amethyst, aventurine, blue quartz, citrine, hawk's eye, pasiolite, prase, quartz cat's eye, rock crystal, rose quartz, smoky quartz, and tiger's eye; the cryptocrystalline quartz gemstones are agate, carnelian, chalcedony, chrysoprase, fossilized wood, heliotrope, jasper, moss agate, onyx, and sard.

Amorphous Silica. Biogenic silica is naturally occurring a-silica from living matter, such as plants and diatoms, radiolarians, or silicoflagellates. Certain species of plants and animals, known as diatoms and radiolarians, respectively, extract dissolved a-silica from their aqueous environment to form structures and shells (USGS 1992). Diatoms and radiolarians are biological sources of a-silica. The remains of diatoms and radiolarians in sediment can harden into diatomite and radiolarite. Diatomite, which is also known as Kieselguhr or diatomaceous earth, is a loosely coherent, chalk-like sediment that contains up to 94% SiO_2 (0.1–4.0% c-silica) (IARC 1987). Aluminum oxide, iron (III) oxide, titanium dioxide, and calcium, magnesium, sodium, and potassium ions are common impurities in diatomite (IARC 1997). High-temperature calcined and high-temperature flux-calcined diatomaceous earth may contain cristobalite, formed during the calcination process of diatomaceous earth (Mossman and Glenn 2013). Flux-calcined diatomaceous earth is produced when diatomite is heated with flux and typically contains between 40 and 60% cristobalite (OSHA 2013c).

Raw diatomaceous earth is obtained through open pit mining (Checkoway et al. 1993). In 2014, an estimated 800,000 tons of diatomite was produced at 11 mining areas and 9 processing facilities in California, Nevada, Oregon, and Washington (USGS 2015). In 2015, national aggregate production volumes were 50,000,000–100,000,000 pounds for raw diatomaceous earth and 500,000,000–750,000,000 pounds for flux-calcined diatomaceous earth (CDR 2017). The estimated world mine reserves of diatomite is large (>360 million metric tons). In 2014, total (world) mine production was 2.36 million metric tons, with 800,000 metric tons in the United States, 430,000 metric tons in China, and 325,000 metric tons in Denmark. The largest diatomite deposits in the world are located in Lompoc, California (Florke et al. 2008). Diatomites are also mined in Georgia, Mississippi, Nevada, Oregon, and Washington.

Vitreous silica (or fused silica), also known as volcanic or silica glass, can be formed naturally by the fusion of siliceous earth following volcanic eruptions, lightning strikes, or meteorite impact (Arts et al. 2007; Fruijtier-Polloth 2012). This glassy silica can also be formed intentionally or unintentionally during certain industrial processes when c-silica is melted and rapidly cooled, preventing recrystallization (Florke et al. 2008; Fruijtier-Polloth 2012; Merget et al. 2002; IARC 1997; Smith 2006). Vitreous silica is also formed by vapor-phase hydrolysis of silicon tetrachloride in a methane oxygen flame. Transparent fused silica is formed from exposing 15 nm silica particles to 1,200°C and 13.8 MPa (2,000 psi) or by electric arc fusion of pure silica sand (Waddell 2006). Silica fume is also a form of a-silica that is generated unintentionally during some metallurgic processes, such as manufacture of ferrosilicon and silicon. (Fruijtier-Polloth 2012; IARC 1997). This method of silica fume generation can be used to intentionally form silica fume to be used in certain manufacturing processes (Florke et al. 2008). Silica fume is not the same as synthetic fumed (or pyrogenic) a-silica, which is discussed below. Both vitreous silica and silica fume often contain small amounts of c-silica (Arts et al. 2007; IARC 1997; Merget et al. 2002). In 2015, national aggregate production volumes of vitreous silica and silica fume were 100,000,000–250,000,000 pounds (CDR 2017).

Synthetic a-silicas are intentionally manufactured forms of a-silica with high purity and generally no detectable amounts of c-silica. There are two main processes, a thermal process (pyrogenic silica) and a wet process (silica gel, precipitated silica, colloidal silica) (Fruijtier-Polloth 2012; Merget et al. 2002). Synthetic a-silica products are often surface-treated to create hydrophobic compounds such as silica dimethicone silylate or silica silylate. The highest synthetic a-silica production capacity in 2004 was in Europe (36%), followed by North America (26%), China (25%; estimated), and Japan (13%) (Waddell 2006). National aggregate production volumes specifically reported for pyrogenic a-silica and a-silica gel were 1,000,000–10,000,000 pounds in 2015 (CDR 2017). For precipitated a-silica, national aggregate production volumes were 498,843,155 pounds in 2011 (CDR 2014); production volume data were withheld in 2012–2015 (CDR 2017). Since colloidal silica does not have a unique CASRN, specific production volume data are not available.

Pyrogenic (or fumed) silica is typically >99.8% silica (IARC 1997). It is prepared by combustion of a volatile silica at temperatures ranging from 1,200 to 2,000°C or oxidizing organic or inorganic silicon compounds (Fruijtier-Polloth 2012; IARC 1997; Waddell 2006). Precipitated silica and silica gel are finely divided synthetic a-silica produced by precipitation from a vapor or solution (EPA 1996). The precipitates are filtered, washed, and dehydrated, which reduce metal oxide impurities to 100–1,000 ppm (Fruijtier-Polloth 2012; IARC 1997). Changing parameters during these processes allows for control of physical parameters, including porosity, pore size, and surface area. Precipitated silica have a broad meso-macroporous pore structure, while silica gels are hydrous silica with an interconnected random array of spheroidal particles with a narrow microporous or mesoporous structure and average pore diameters of 2–50 nm (Florke et al. 2008; Fruijtier-Polloth 2012). Silica gel is produced when aqueous alkali metal silicate is neutralized under acidic conditions, initiating the polymerization of a-silica into small spheroids. Silica gel has three variations referred to as hydrogel, aerogel, and xerogel based on the production method used (Waddell 2006). Colloidal silica is produced in a manner similar to silica gel; however, SiO_2 concentrations are kept low (10–15%) and the pH is maintained at a slightly alkaline level during production. This allows the subunits to stay separate and form a stable dispersion (Fruijtier-Polloth 2012). The suspension is stabilized chemically (e.g., KOH, NaOH, NH_3, HCl) or via electrostatic repulsion of particles (substitution of some silica atoms with aluminum) (Fruijtier-Polloth 2012). A different process, known as the Stöber method, is used to create stabilized suspensions spherical colloidal a-silica nanoparticles using controlled growth of particles following hydrolysis of alkylsilicates with condensation of silicic acid in an ethanolic solution with catalytic amounts of ammonia (Fruijtier-Polloth 2012, 2016).

Primary particles formed during the manufacture of synthetic a-silicas are in the nanometer range, but covalently bond during production to form indivisible SiO_2 aggregates >100 nm. These aggregates can further combine to form micron-sized agglomerates (Fruijtier-Polloth 2012, 2016; Merget et al. 2002; Taeger et al. 2016). With the exception of colloidal silica, primary nanosized particles do not exist in commercial products. However, colloidal dispersions have been shown to contain stable isolated nanoparticles in addition to aggregates in the respirable range (Fruijtier-Polloth 2012, 2016).

5.2.2 Import/Export

Chrystalline Silica. In 2012, 306,000 metric tons of industrial sand were imported into the United States and 4.36 million metric tons were exported. The largest quantities of industrial sand and gravel imported were from Canada (226,000 metric tons) and Mexico (64,000 metric tons) (USGS 2014b). The largest quantities of industrial sand and gravel exported were from the United States to Canada (2.33 million metric tons), Mexico (807,000 metric tons), and Japan (632,000 metric tons). In 2013, 160,000 metric tons of industrial sand were imported into the United States and 2.96 million metric tons were exported.

In 2013, 3 million metric tons of construction sand were imported into the United States (USGS 2015). The largest quantities of construction sand and gravel imported were from Canada (2.37 million metric tons), Mexico (210,000 metric tons), the Bahamas (150,000 metric tons), and other (270,000 metric tons).

Amorphous Silica. In 2014, 3,000 tons of diatomite were imported for use and 87,000 tons were exported (USGS 2015). Imports were from Mexico (1,080 metric tons), France (990 metric tons), China (300 metric tons), and others (630 metric tons). Several manufacturers reporting use of vitreous silica and silica fume in 2015 indicated that the compound was imported; however, the imported volume was withheld (CDR 2017). Similarly, most manufacturing companies withheld export volumes; however, two companies reported 14,000 and 55,704 pounds of exported vitreous silica and one company reported 596,000 pounds of exported silica fume in 2015 (CDR 2017).

Import/export information on precipitated, pyrogenic, and gel a-silica compounds is available from the Chemical Data Reporting Submissions Database (CDR 2017). Several manufacturers reported use of imported precipitated, pyrogenic, and gel a-silica. Reported import volumes of 26,824–1,523,405 pounds were reported for precipitated a-silica by four manufacturers; however, most companies indicated that import volume data were confidential business information (CBI). For pyrogenic a-silica and a-silica gel, all imported volume data were withheld by manufacturers. Two manufacturers reported export volumes of 27,108 and 2,596,136 pounds for pyrogenic a-silica. Export volume data for precipitated a-silica and a-silica gel were either CBI or withheld.

Colloidal silica is imported primarily from Wales, with small amounts from Japan (amounts not reported). Exporting of colloidal silica is approximately 1,800 metric tons, primarily to Japan, Taiwan, and Canada, with some exports to Western Europe (Florke et al. 2008).

5.2.3 Use

Chrystalline Silica. Sand and gravel are used for road building and concrete construction (OSHA 2013c). In the United States, an estimated 44% of construction sand and gravel is used for concrete aggregates; the remainder is used for road base and coverings and road stabilization (25%), asphaltic concrete aggregates and other bituminous mixtures (13%), construction fill (12%), concrete products (1%), plaster and gunite sands (1%), snow and ice control (1%), and filtration, golf courses, railroad ballast, roofing granules, and other miscellaneous uses (3% combined) (USGS 2015).

Heavy industry uses quartz sand to produce high-temperature or refractory silica brick, foundry molds, and cores for the production of metal castings (IARC 2012). The oil and gas industry uses a water-sand mixture to fracture rock. Silica sand is used as a proppant, to prop open fractures and promote hydrocarbon flow and extraction. Water and proppants make up 98–99.5% of typical fracturing fluids. Silica sand with a round spherical shape and commonly graded particle distribution is specifically selected for hydraulic fracturing fluid production. Resin-coated silica is also used as a proppant (Holloway and Rudd 2014). In the United States, an estimated 72% was used as hydraulic fracturing sand

and well-packing and cementing sand; the remainder was used for glassmaking sand (13%), foundry sand (6%), whole-grain fillers and building products (3%), other whole-grain silica (2%), ground and unground sand for chemicals (2%), and other uses (2%) (USGS 2015). c-Silica is used as an asphalt filler and in bricks, mortar, plaster, caulk, roofing granules, wallboard, concrete, and dimension stone in building materials (IARC 2012). Quartz is used as filler in plastics, rubber, and paint or as an abrasive (e.g., blasting, scouring cleansers, sawing, and sanding). Quartz sand is used in municipal water filter beds and sewage treatment plants for filtering out impurities, sediment, and bacteria. Sand and gravel aggregates are used as abrasives on roads in winter (EC 2013).

c-Silica is used in products such as art clay, glazes, cleansers, cosmetics, pet litter, furniture foam, personal care products, talcum powder, and Jeweler’s rouge (buffing agent) and as a gemstone (e.g., amethyst, citrine, and quartz) (IARC 2012; USGS 1992). Silica gemstones are used in jewelry, for collections, decorative art objects, and exhibits (USGS 2014a). Cristobalite sand, powder, and flour are used in the production of plastics, adhesives, wall paint, texture coatings, and road paint (Florke et al. 2008).

Quartz sand is used to manufacture glass and pure silicon for computer chips. Sand with >98% silica content is used for glass and ceramics. Finely ground c-silica is used to make ceramics (e.g., pottery, brick, and tile), porcelain, and fine china (IARC 2012; USGS 1992). Windows and specialized devices such as lasers use optical-grade quartz, while electronic-grade quartz is required for electronic circuits. Electronic-grade quartz crystal is used for accurate filters, frequency controls, and timers used in electronic circuits (USGS 2014b). Piezoelectric quartz crystals convert mechanical pressure into electricity and are used in advanced communication systems (IARC 2012; USGS 1992).

Silica stone, a type of c-silica, is produced to manufacture files, deburring-tumbling media, oilstones, and whetstones (USGS 2014b). Artificial, decorative stone products for bathroom and kitchen countertops are manufactured with up to 93% silica content (Kramer et al. 2012). Quartzite, tripoli, ganister, chert, and novaculite are commercially produced silica products (NTP 2014).

Tripoli is extremely fine-grained c-silica, used as a functional filler and extender in adhesives, plastics, rubber, and sealants, and in toothpaste, tooth polishing compounds, industrial soaps, metal- and jewelry-polishing compounds, and buffing and polishing compounds for lacquer finishing in the automobile industry (OSHA 2013c; USGS 2014b). Silica flour (CASRN 14808-60-7) is a fine grade of silica with particles up to 100 μm in diameter used in toothpaste, scouring powders, metal polishes, paints, rubber, paper, plastics, wood fillers, cements, road surfacing materials, and foundry applications (NIOSH 1981; NTP 2009).

Amorphous Silica. Diatomite is used for removing microbial contaminants (e.g., bacteria, protozoa, and viruses) in public water systems (USGS 2015). In 2014, diatomite was used predominantly in filter aids (58%), absorbents (14%), cement (14%), and fillers (13%), and for other specialized applications such as pharmaceutical and biomedical uses (1%). Diatomaceous earth silica and silica gel are used as insecticides and acaricides to control insects, mites, and ticks (EPA 1991). The particle size of diatomaceous earth influences the insecticidal efficacy (Vayias et al. 2009). These compounds act as pesticide carriers and abrasive desiccants, which remove oily, protective films causing insects to dry out and die. Diatomite is applied to stored grain, food stores, feed, and ornamental plants, as well as on pets and their living or sleeping areas.

Silica fume, a-silica formed as a byproduct of silicon metal or ferrosilicon alloy production, is used in cement, concrete, and mortars to improve strength and durability (Florke et al. 2008). Transparent and nontransparent vitreous silica glass is used in tubing, rods, crucibles, dishes, boats, chromatographic substrate, precious-metal thermocouples protection, high temperature pyrometry prisms, lenses, cells, windows, other optical components, lasers, mercury vapor lamps, transducers, semiconductor technology, space shuttle windows, and optical fibers (Smith 2006).

Synthetic a-silicas, in particular silica gel compounds, are approved for use as food additives and in food packaging (FDA 2015a, 2015b; Fruijtier-Polloth 2012, 2016). The potential for a-silica migration into food from packaging will depend on the degree to which it is encapsulated into the packaging matrix (Stormer et al. 2017). They are also used as anti-caking agents and excipients in pharmaceuticals and dietary supplements (Fruijtier-Polloth 2012, 2016; IARC 1997; Merget et al. 2002). Silica gel is used as a desiccant and adsorbent for water and other species, thickener in dentifrice, matting agent in coatings, chromatographic media, and catalyst support (Florke et al. 2008; IARC 1997). Silica gel is also used as insecticides and acaricides to control insects, mites, and ticks (EPA 1991).

Various a-silica compounds are also used in cosmetics such as makeup preparations, hair dyes and colors, hair bleaches, hair straighteners, permanent waves, hair preparations, toothpaste, personal cleanliness products, skin care preparations, bubble baths, bath oils, tablets, and salts, body and hand preparations (excluding shaving preparations), moisturizing preparations, underarm deodorants, paste masks, perfumes, foot powders and sprays, cleansing products, and suntan gels, creams, and liquids (Florke et al. 2008; Fruijtier-Polloth 2016).

Pyrogenic a-silicas are used in silicone rubber reinforcement, heat insulation, and as thickeners and anti-setting agents in liquid coatings, adhesives, inks and toners, undercoatings, and fire extinguishers (IARC 1997; Merget et al. 2002).

The primary use for colloidal silica is in investment casting (e.g., in production of jet engine components) (Florke et al. 2008). Colloidal silica can also be used in the production of refractory fibers, paper, and fibrous ceramics; to increase the strength and adhesion of paints and adhesives; for paper and cardboard frictionizing; as antisoil coating for carpets and other surfaces; and to polish silicon wafers (Florke et al. 2008; Lee and Kelly 1992). Colloidal silica can be used to increase the strength and adhesion of paints and adhesives (Florke et al. 2008). Beverages, including wine, beer, and fruit juices, can be clarified using colloidal silica (Florke et al. 2008).

5.2.4 Disposal

In the United States, approximately 34% of glass containers are recycled (USGS 2015). Foundry sand and cullet or glass pieces are also recycled, but to a lesser extent. Asphalt road surface layers, cement concrete surface layers, and concrete structures are recycled; however, it is considered to be a small percentage of aggregate (or total) amount used. Approximately 13.7 kg of Portland cement concrete was recycled in 2012 (USGS 2014c).

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 2005). 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 is included in Standard Industrial Classification (SIC) Codes 10 (except 1011, 1081, and 1094), 12 (except 1241), 20–39, 4911 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4931 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4939 (limited to facilities that combust coal and/or oil for the purpose of generating electricity for distribution in commerce), 4953 (limited to facilities regulated under RCRA Subtitle C, 42 U.S.C. section 6921 et seq.), 5169, 5171, and

7389 (limited S.C. section 6921 et seq.), 5169, 5171, and 7389 (limited to facilities primarily engaged in solvents recovery services on a contract or fee basis); and if their facility produces, imports, or processes ≥25,000 pounds of any TRI chemical or otherwise uses >10,000 pounds of a TRI chemical in a calendar year (EPA 2005).

5.3.1 Air

There is no information on releases of silica to the atmosphere from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005).

Crystalline Silica. c-Silica may be released to air by natural and human processes. c-Silica is emitted into the ambient environment as a component of particulate emissions (EPA 1996). Process-stream air emissions of c-silica occur during activities, such as brick making, and fugitive emissions of c-silica occur ancillary to activities. For example, soil particles containing c-silica enter the atmosphere when vehicles travel on unpaved roads as fugitive emissions. Ambient dust containing silica by fugitive emissions include agricultural tilling, construction, mining, quarrying, hydraulic fracturing, paved and unpaved roads, and wind erosion sources. Soil geology factors are an important source of variability in c-silica emissions by fugitive releases in construction.

There are multiple possible sources of ambient c-silica. Industrial quarrying and mining are inherently dusty and are expected to contribute to ambient c-silica emissions (EPA 1996). c-Silica may be released during metallurgic manufacturing, although this is dependent on the c-silica use and application of particulate pollution control efforts. Power plant emissions contain c-silica from spent ash and combustion (EPA 1996). Sanding roads for deicing activities in winter may be a potential exposure route for c-silica as particulate emissions (EPA 1996).

Cristobalite dust may become released into the air by volcanic eruptions (OSHA 2013c). Forest fire and crop burning may release c-silica, as original a-silica in vegetation may release c-silica (cristobalite and quartz) when burned at high temperatures (EPA 1996). Wind erosion emissions of silica, where particulate aerosols are generated from air currents moving over soil, may spread c-silica particles in soils, and vary based on soil parameters, climatic factors, geographic features, vegetation type, and farming practices (EPA 1974).

In urban areas across the United States, the measured mean 24-hour average ambient c-silica concentration ranged from 0.0009 to 0.008 mg/m^3 for particles in the size range of 2.5–5 µm, as presented in Table 5-1 (EPA 1996). The mass median aerodynamic diameters (MMADs) of most c-silica particles released into the environment were >2.5 µm. Average ambient levels of c-silica with <15 µm aerodynamic diameter in metropolitan areas of the United States generally have ranged between 0.001 and 0.003 mg/m^3 in most circumstances and are not expected to exceed an annual average of 0.008 mg/m^3 (EPA 1996).

Table 5-1. Average Quartz Concentrations in Ambient Air for Sites in 22 U.S. Cities—Dichotomous Samples

		Coarse quartz (µg/m^{-3})		Fine quartz (µg/m^{-3})		TDM[a] (µg/m^{-3})		Quartz percentage of TDM[a]	
Site[b]	N[c]	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Coarse	Fine
Akron, OH	7	4.2	1.4	<0.1	0.1	71.2	16.1	5.9	<0.1
Boston, MA	1	8.0	–	0	–	140.8	–	5.7	0
Braidwood, IL	1	4.4	–	0	–	57.2	–	7.7	0
Buffalo, NY	14	2.3	1.4	0.1	0.3	83.6	26.6	2.8	0.1
Cincinnati, OH	2	2.6	1.5	0	–	63.2	1.0	4.1	0
Dallas, TX	4	2.6	1.0	0.3	0.3	62.7	22.9	4.2	0.5
El Paso, TX	10	2.2	1.1	0.1	0.1	76.5	43.2	2.9	0.1
Five Points, CA	3	6.6	3.2	1.0	1.2	124.8	84.1	5.3	0.8
Hartford, CT	2	3.0	2.1	0	–	54.8	6.2	5.5	0
Honolulu, HI	1	1.2	–	1.2	–	47.1	–	2.6	2.6
Inglenook, AL[d]	8	5.2	1.7	0.3	0.2	72.6	14.0	7.2	0.4
Kansas City, KS	8	4.7	2.6	0.4	0.4	69.2	28.3	6.8	0.6
Kansas City, MO	3	4.2	3.0	0.1	0.1	58.6	21.6	7.2	0.2
Minneapolis, MN	6	3.7	2.3	0.1	0.1	46.5	7.9	8.0	0.2
Portland, OR	7	1.4	0.6	<0.1	0.1	133.9	122.2	1.0	<0.1
Research Triangle Park, NC	3	0.9	0.5	0.4	0.1	37.0	3.5	2.4	0.1
Riverside, CA	4	3.0	1.1	0	–	106.6	42.2	2.8	0
St. Louis, MO	5	4.4	2.6	0.1	0.1	57.0	11.5	7.7	0.2
San Jose, CA	6	1.9	0.9	<0.1	0.1	67.0	27.3	2.8	<0.2
Seattle, WA	1	1.0	–	0.1	–	36.1	–	2.8	0.3

Table 5-1. Average Quartz Concentrations in Ambient Air for Sites in 22 U.S. Cities—Dichotomous Samples

		Coarse quartz ($\mu g/m^{-3}$)		Fine quartz ($\mu g/m^{-3}$)		TDM[a] ($\mu g/m^{-3}$)		Quartz percentage of TDM[a]	
Site[b]	N[c]	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Coarse	Fine
Tarrant, AL[d]	6	4.3	2.3	1.9	1.0	101.9	57.7	4.2	1.9
Winnemucca, NV	5	5.9	4.3	0.8	0.7	65.7	47.4	9.0	1.2

[a] Total dichotomous mass.
[b] Post office state abbreviations used.
[c] Number of filters analyzed.
[d] North Birmingham.

Source: EPA 1996

Green et al. (1990) evaluated agricultural particulate emissions and background emissions using regional historical data in Alberta, Canada. Variability was associated with the farm and the crops raised. Background total suspended particulate levels ranged from 0.040 to 0.080 mg/m^3, with 0.85–17.5% c-silica.

PM_{10} concentrations obtained 22–745 m downwind from a sand and gravel facility in California ranged from approximately 0.026 to 1.026 mg/m^3 (Shiraki and Holmen 2002). The airborne quartz mass concentrations from the three downwind sites ranged from 0.0262 to 0.0972 mg/m^3. Samples obtained at one site 1,495 m upwind had mass concentrations of quartz ranging from 0.0041 to 0.0163 mg/m^3.

In another study, the measured ambient concentrations of PM_4 c-silica ranged from below the detectable limit (0.0003 mg/m^3) to 0.0028 mg/m^3 in samples collected upwind and downwind of quarry and processing equipment at Carroll Canyon and Vernalis plants in California (Richards et al. 2009). The 8-hour working shift PM_{10} c-silica concentrations ranged from 0.001 to 0.0109 mg/m^3. The study was sponsored by the National Stone, Sand, & Gravel Association and samples were collected downwind of four crushing plants processing high-quartz-content rock (Richards et al. 2009).

Recent air monitoring reports conducted by the Minnesota Air Pollution Authority evaluated c-silica in PM_{10} and PM_4 particles in ambient air near industrial sand mining, processing, and transport sites (MPCA 2015a, 2015b). For PM_{10} particles, almost all measurements were below the detectable limits (0.001 mg/m^3), with all values <0.002 mg/m^3 (MPCA 2015a).

For PM_4 particles, almost all measurements were below the detectable limits (0.0012 mg/m^3), with all concentrations <0.007 mg/m^3 (MPCA 2015b). Air monitoring in downtown Winona, Minnesota showed that the c-silica concentration was <0.0005 mg/m^3 in all samples (MPCA 2015c).

Amorphous Silica. Data on a-silica releases into the air are limited, as most monitoring studies focus on c-silica (EPA 1996). a-Silica from diatomaceous earth can be released into the air at processing plants. Respirable dust concentrations for raw, calcined, and flux-calcined diatomaceous earth were reported to be <1.05, 0.21, and 0.14 mg/m^3, respectively, at a U.S. processing plant. c-Silica fraction of respirable dust was <1, 10–20, and 40–60%, respectively (IARC 1987). In a Swedish plant, respirable dust concentrations ranged from 0.1 to 2.0 mg/m^3, with c-silica fraction ranging from 5% in raw diatomite to 75% in calcined products (IARC 1987).

a-Silica byproducts may be released into the air due to releases of fly ash from power stations and various silicon manufacturing facilities (IARC 1997). In foundries and metallurgical industries that produce these byproducts (e.g., silica fume), the silica content of respirable dust ranged from 0.5 to 66 mg/m^3. Silica dust in these industries are primarily a-silica, but may contain up to approximately 20% c-silica (IARC 1987).

When crops (e.g., sugarcane) and non-crop vegetation are burned (e.g., forest fire), biogenic a-silica fibers are released. As discussed above, at high temperatures, burning vegetation may release c-silica (cristobalite and quartz) (EPA 1996; IARC 1997; Le Blond et al. 2010). Biogenic a-silica can also be released from sugarcane and rice crops during harvesting, transporting, and/or milling (IARC 1997).

According to the Ecotoxicology and Toxicology of Chemicals Joint Assessment of Commodity Chemicals report (ECETOC 2006), synthetic a-silica, primarily precipitated and gel a-silica, may be released into the air in small amounts during the manufacturing process, at an estimated rate of 0.438 kt SiO_2/year. Total dust concentrations reported in a German synthetic pyrogenic a-silica plant were 2–7 mg/m^3 (IARC 1987).

5.3.2 Water

There is no information on releases of silica to water from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005).

c-Silica and biogenic a-silica particulates are naturally present in water as quartz and diatom fragments, with much higher levels of c-silica particulates compared with a-silica (IARC 1987, 1997; Trėguer and De La Rocha 2013). Silicon dissolves from minerals in water, forming bioavailable silicic acid, $Si(OH)_4$ (Lickiss 2006). c-Silica is virtually insoluble in water; however, dissolved silica flows from rivers and groundwater into the ocean where it may settle into marine sediments or be taken up by organisms as part of the biogeochemical silica cycle (Trėguer and De La Rocha 2013). a-Silica is poorly soluble, but as it is more soluble than c-silica (see Section 4.2), biogenic a-silica is the primary source of dissolved silica (Ning 2002). The term 'dissolved silica' (dSi) corresponds to silicic acid, which is formed from inorganic silicon dissolving from lithogenic sources, such as silicate minerals, as part of the weathering process. This weathering process is considered to be the greatest source of silica in aquatic ecosystems (Sferratore et al. 2006). The transformation and degradation of silica in water is further discussed in Section 5.4.2. Quartz sand is added to municipal water filter beds and sewage treatment plants for filtering out impurities, sediment, and bacteria (IARC 1987). According to the European Centre for Ecotoxicology and Toxicology of Chemicals Joint Assessment of Commodity Chemicals report (ECETOC 2006), synthetic a-silica, primarily precipitated as gel a-silica, may be released into the water in small amounts during the manufacturing process, at an estimated rate of 2.1 kt SiO_2/year.

5.3.3 Soil

There is no information on releases of silica to soil from manufacturing and processing facilities because these releases are not required to be reported (EPA 2005).

Silica is a natural component of sediments, soils, and rock-forming minerals in magmatic and metamorphic rocks (Florke et al. 2008; IARC 1987, 1997). Quartz is present in trace to major amounts in sedimentary (e.g., sandstones and conglomerates) and metamorphic rock types (IARC 2012), and diatomite deposits are found worldwide (Florke et al. 2008). Silicon dioxide (diatomaceous earth) and silica gel are released to soil as registered pesticides for use on food and nonfood crops (EPA 1991). Biogenic a-silica is released into the soil after burning or natural decomposition of plants and crops (IARC 1997).

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

Quartz, cristobalite, and tridymite are found in rocks and soil and can be released to the environment through natural processes, such as weathering or volcanic eruptions, and from anthropogenic sources, such as foundry processes, brick and ceramics manufacturing, silicon carbide production, burning of agricultural waste or products, or calcining of diatomaceous earth (IARC 2012). At least a trace amount of c-silica, in the form of quartz, is present in all soils (USGS 1992). Quartz is the major component of sand and dust particulate matter in air.

Both c- and a-silica particles may be transported by wind or water currents as part of the biogeochemical silica cycle. Dissolved silica is transported by river and groundwater sources into the ocean. Ocean water also contains silica from dissolution of terrestrial lithogenic silica in marine sediments, Aeolian dust settling on the ocean water surface, and weathering of continental rocks (Trėguer and De La Rocha 2013). a-Silica deposits may settle out of water into sediment from biogenic sources. c-Silica may undergo atmospheric transport as a fractional component of particulate emissions (EPA 1996).

5.4.2 Transformation and Degradation

Natural or synthetic changes in temperature and pressure may cause the crystalline structure of silica to change (IARC 2002). At elevated temperatures, the silica tetrahedron linkages break and reform into new crystalline structures (OSHA 2013c). Quartz, the most common form of c-silica, converts to cristobalite at 1,470°C, and cristobalite loses its crystalline structure and becomes amorphous fused silica at 1,723°C. The temperature-dependent transitions reverse at extremely slow rates. Different forms of silica co-exist after the heated silica crystal cools. At lower temperatures, the silica-oxygen bonds in the silica tetrahedron rotate or stretch, causing alpha and beta transitions that are readily and rapidly reversed upon cooling. Cristobalite and tridymite are formed when quartz or a-silica is subjected to extremely high temperatures (Leung et al. 2012; Mossman and Glenn 2013). Biogenic a-silicas are converted into cristobalite at approximately 800°C (IARC 1997). Cristobalite is produced when natural a-silica diatomaceous earth (diatomite) is heated with or without flux, resulting in cristobalite fractions of 10–20% in calcined product and 40–60% in flux calcined product (IARC 1987, 1997; OSHA 2013c).

Natural activities may cause silica polymorph transformations. For example, lightning strikes or meteorite impacts can change alpha quartz into keatite or coesite (IARC 2002), or vitreous silica (a-silica glass) may form under these conditions from the fusion of siliceous materials in soil (IARC 1997). Cristobalite may be produced by combustion metamorphism of naturally occurring substances (e.g., bituminous rocks, coal, or oil) (Clark and Peacor 1992). Anthropogenic activities may also cause transformation of silica from one polymorph into another (IARC 2012). Quartz in furnace bricks may convert to cristobalite when subjected to prolonged high temperatures. Burning of agricultural wastes, such as rice hulls, or forest fires may also cause a-silica to convert to cristobalite.

Air. Little information is available on the atmospheric reaction of silica. The c- and a-silica forms found in air as dusts are stable and not subject to photochemical reactions.

Water. Silicon dissolves from minerals in water forming bioavailable silicic acid ($Si(OH)_4$) reaching concentrations <2 mM at near neutral pH (Lickiss 2006). Silicic acid polymerization rate is dependent on temperature, ionic strength of the solution, pH, and silica saturation. Polymerization is fast in neutral and slightly alkaline solutions, and slow at pH values of 2–3 (Icopini 2005; Ning 2002). For example, silica polymerization rates were evaluated at 25°C in a series of controlled experiments. The reported fourth-order rate constants for the 0.01 molal ionic strength experiment with an initial concentration of 20.8 mmolal were $1.17\text{x}10^{-9}$ $\text{millimolal}^{-3}\cdot\text{second}^{-1}$ at pH 3 and $3.53\text{x}10^{-10}$ $\text{millimolal}^{-3}\cdot\text{second}^{-1}$ at pH 11 (Icopini 2005). Soluble silica half-lives were reported to be approximately 355 minutes at pH 6.5, 55 minutes at pH 8, and 95 minutes at pH 8.75 (Zuhl and Amjad 2013). a-Silica is more soluble than c-silica; therefore, the primary source of dissolved silica in natural waters is biogenic a-silica (Ning 2002). The portions of c-silica and biogenic a-silica that do not dissolve settle into the sediment. Cycling between silica particles and dissolved silica occurs at the sediment-water interface (Tréguer and De La Rocha 2013; Tréguer et al. 1995). Additionally, dissolved silica is a source of biogenic a-silica for diatoms, radiolarians, and sponges (IARC 1997). Colloidal silica is non-reactive and stable in fresh water, but can be depolymerized in seawater; polymerized colloidal silica settles into the sediment (Ning 2002).

Sediment and Soil. Quartz is extremely resistant to physical and chemical breakdown by the weathering process (USGS 1992). The weathering rate of a square meter of catchment area from different geographic areas using field measurements is 10^{-2}–10^{-1} $\text{moles}\cdot\text{m}^{-2}\cdot\text{year}^{-1}$ (Ning 2002). Synthetic a-silica compounds are inert, and are not expected to transform or degrade in soil (ECETOC 2006). Terrestrial plants uptake bioavailable forms of a-silica from the soil, particularly grasses (IARC 1997).

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to silica depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of silica 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 silica levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable.

Table 5-2 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 5-3.

Table 5-2. Lowest Limit of Detection Based on Standards[a]

Media	Detection limit	Reference
Air (dust)	c- or a-silica: 5 µg/sample	NIOSH 2003a, 2003c, 2003d
Water (dissolved silica)	10 µg silica/L	EPA 2003; USGS 1987
Soil/sediment	Quartz: <1% of sample or 8 µg/sample	Barredo and Polo Diez 1980; Sheffield 1994; Stopford 1994
Biological samples	c-silica: 10 µg/sample	NIOSH 2003b

[a] Detection limits based on using appropriate preparation and analytics. These limits may not be possible in all situations.

Table 5-3. Summary of Environmental Levels of Silica

Media	Low	High	Reference
Outdoor air	Urban: c-Silica (0.3–10.5 µM): 0.25 µg/m^3	Urban: c-Silica (0.3–10.5 µM): 2.87 µg/m^3	Bhagia 2009; De Berardis et al. 2007; ECETOC 2006; IARC 1997; Lawson et al. 1995
	Near industrial site: Quartz: 41.07 µg/m^3	Near industrial site: Quartz: 57.22 µg/m^3	
	5 km from industrial site: Quartz:3.51 µg/m^3	5 km from industrial site: Quartz: 3.51 µg/m^3	
	Ambient a-silica: <0.2 µg/m^3	Ambient a-silica: 135 µg/m^3	
	a-Silica near farming operation: <0.004 fibres/mL	a-Silica near farming operation: 0.2 fibres/mL	

Table 5-3. Summary of Environmental Levels of Silica

Media	Low	High	Reference
Indoor air	Near stone crushing site: PM_4=500 µg/m^3 (7–24% c-silica; ~35–120 µg/m^3)	Near stone crushing site: PM_4=650 µg/m^3 (7–24% c-silica; ~46–156 µg/m^3)	Mukhopadhyay et al. 2011
Surface water	Dissolved silica: 0.12 mg/L	Dissolved silica: 6 mg/L	Tréguer et al. 1995
Deep water	Dissolved silica: 0.6 mg/L	Dissolved silica: 10.8 mg/L	Tréguer et al. 1995
Ground water	Dissolved silica: 17 mg/L	Dissolved silica: 17 mg/L	Tréguer et al. 1995
Drinking water	3.3 mg/L	7.1 mg/L	ECETOC 2006; Sferratore et al. 2006
Food (ppb)	Estimated a-silica intake from food: 0.28 mg/kg/day	Estimated a-silica intake from food: 12.7 mg/kg/day	Fruijtier-Polloth 2016
Soil	c-silica: trace a-silica: 3.9 mg/g a-silica: 706 g/kg (dry weight)	c-silica: 95% a-silica: 5.2 mg/g a-silica: 706 g/kg (dry weight)	ECETOC 2006; NTP 2014; Sferratore et al. 2006; USGS 1992

No data are available on levels of silica in air, water, and soil at NPL sites (ATSDR 2017).

5.5.1 Air

Crystalline Silica. Widespread natural occurrence and use of silica-containing materials result in silica-containing airborne dusts being present in the environment (Moore 1999). Silica particles suspended in the air create non-explosive dusts (OSHA 2013c). Silica from unconsolidated material on the earth’s surface in the form of soils, deserts and beaches, volcanic ash, and extraterrestrial dust are natural sources of silica in air (Moore 1999). Remote continental air contains a background gravimetric airborne dust concentration of 0.04 mg/m^3, of which ≥10% is c-silica. Desert dust consists of fine particles (<10 µm) of quartz (IARC 1997).

Samples collected from an urban area in Rome, Italy between September 2004 and October 2005 were analyzed to determine the concentration of silica particles in the inhalable particulate fraction (De Berardis et al. 2007). The total PM10 particulate in the samples contained 1.6±0.6–10.4±1.4% silica or 0.00025–0.00287 mg c-silica/m^3 air. The silica particles in the samples had a mean diameter range of 0.3–10.5 µm, and >87% had a diameter of <2.5 µm. The authors hypothesized that Southern winds from the Sahara Desert carry silica particles into Mediterranean Europe. Corresponding data on the intensity and direction of the wind, humidity, and rain on and near sampling days demonstrated a strong relationship between the concentration of c-silica in the samples and meteorological-climate conditions. The weight percent of c-silica in particles was higher between April and June than the winter months.

The concentration of quartz was reported to be ≤0.034 mg/m^3 in air samples from Tokyo in 1965. The concentration of cristobalite and potential sources of airborne silica were not reported (NTP 2009). Dust samples collected from two communes in a sandy area of Gansu Province, China during the windy season ranged from 8.35 to 22 mg/m^3. The dust consisted of fine particles (<5 μm) with a free silica content of 15–26% (IARC 1997).

Volcanic ash collected at 34–36 km altitude from El Chichón (Mexico) were composed of 35% cristobalite and keatite. Volcanic ash collected from Mount St. Helens in Washington State contained 3–7% c-silica (IARC 1997).

Air monitoring was performed using PM_{10} high volume samplers at two locations near an industrial slate pencil site and at one control site 5 km away (Bhagia 2009). The quartz concentrations were 0.04107±0.02125–0.05722±0.02205 mg/m^3 near the slate industrial site and 0.00351±0.00145 mg/m^3 at the control site. In another study, PM_{10}, PM_4, and $PM_{2.5}$ ambient air samples were obtained for indoor air in two villages neighboring stone crushing sites in India (Mukhopadhyay et al. 2011). The silica content in the samples was between 7 and 24%. The average ambient PM_{10} values in the two neighboring communities were 0.77 and 0.46 mg/m^3. The indoor air average PM_4 values were 0.5 and 0.65 mg/m^3, respectively, and the $PM_{2.5}$ values were 0.13 and 0.28 mg/m^3, respectively. The workers' average exposure to respirable particulates (PM_4) in three stone crushing units ranged from 4.51 to 8.15 mg/m^3 (Mukhopadhyay et al. 2011).

Amorphous Silica. According to the European Centre for Ecotoxicology and Toxicology of Chemicals Joint Assessment of Commodity Chemicals report (ECETOC 2006), ambient a-silica levels in the air range from <0.2 to 135 μg/m^3. In California, 1 of 11 samples obtained upwind of rice farming operations and half of the downwind samples contained a-silica at a concentration of 0.02 fibers/mL; the overall mean concentration of all downwind samples was 0.004 fibers/mL. Silica fibers (fiber length in the respirable dust fraction: >5 μm, with 90% of fibers <5 μm in length; range of fiber width: 0.2–75 μm), measured by polycarbonate membrane filter, were detected in 4 of 14 samples in neighboring towns on days when there was rice burning at a mean concentration of <0.004 fibers/mL (Lawson et al. 1995). a-Silica fibers were identified in three of seven smoke samples collected near burning sugarcane fields in Hawaii (IARC 1997).

5.5.2 Water

Silicon dissolves from natural sources of c- and a-silica in water, forming bioavailable silicic acid, $Si(OH)_4$, reaching concentrations up to 2 mM at near neutral pH (Lickiss 2006). a-Silica is more soluble than c-silica (see Section 4.2); therefore, the primary source of dissolved silica is biogenic a-silica (Ning 2002). Ning (2002) reported typical concentrations of silica in natural waters of 13 ppm for lakes, 3–15 ppm for major rivers, 1–10 ppm for seawater, 2–60 ppm for wells, and 50–300 ppm for wells in volcanic and oil fields (Ning 2002). Tréguer et al. (1995) reported average dissolved silica concentrations of 9 mg/L in rivers, 4 mg/L in lakes, and 17 mg/L in groundwater. The average reported concentration of dissolved silica in ocean waters, nearly exclusively in monosilicic acid form, was 4.2 mg/L, with low concentration at the surface (0.12–6 mg/L) and higher concentrations in deep and bottom waters (0.6–10.8 mg/L) (Tréguer et al. 1995).

Median seasonal concentrations of silica were reported for 12 sites in the Hudson River Basin in New York State (Wall et al. 1998). The samples taken between December and March had silica concentrations ranging from 2.8 to 10.0 mg/L. The samples collected between April and November had silica concentrations ranging from 0.72 to 9.1 mg/L. George et al. (2000) measured the total silica content in springs and wells in Southern Nevada. Total silica concentrations were detected for the low molecular weight silica that were not colloidal. The authors suggested that decreases in the silica concentration was due to biological causes, such as phytoplankton uptake, based on silica concentrations correlating to the nitrate concentration trend.

According to the European Centre for Ecotoxicology and Toxicology of Chemicals Joint Assessment of Commodity Chemicals report (ECETOC 2006), U.S. drinking water contains a median dissolved silica concentration of 7.1 mg/L. In the Seine River watershed, the average a-silica concentration in tap water and two water treatment plants was 4.1 mg/L (Sferratore et al. 2006).

5.5.3 Sediment and Soil

Crystalline Silica. Silica is ubiquitous in the environment; over 95% of the earth's crust is made of silica-containing minerals and c-silica (Uhrlandt 2006). c-Silica has been found in samples from every geologic era and from every location around the globe (USGS 1992). Alpha quartz is most common in nature, accounting for almost 12% by volume of the earth's crust (OSHA 2013c). At least a trace amount of c-silica, in the form of quartz, is present in all soils. Quartz is found as crystals, aggregates, or discrete particles (IARC 1997). The silica polymorphs, cristobalite and tridymite, are found in rocks, soil, and volcanic rocks. Volcanic rocks in California and Colorado are a major source of cristobalite and tridymite in the United States (NIOSH 1986). The c-silica polymorphs keatite, coesite, stishovite, and moganite are rarely found in nature (IARC 2012).

Quartz is an important component of many igneous and sedimentary rocks (IARC 1997). The sedimentary rocks sandstones, greywackes, and shales contain 82, 37, and 20% quartz by weight, respectively. Some of the igneous rocks that contain quartz are rhyolites, alkali granites, alkali rhyolites, and granites in 33.2, 32.2, 31.1, and 29.2% quartz by weight, respectively. Typically, silica sand deposits have a silica content of 95%, although impurities may reach up to 25% (NTP 2014).

Soils from North Carolina were analyzed for quartz content (Stopford and Stopford 1995). Sandy-loam soils with particles in the 4.25 µm fraction had an average quartz content of 15.2%, clay soils had 2.2%, and sandy soils had 31.6%. Quartz was detected in dust samples collected from indoor and outdoor locations in Oman (Abdul-Wahab et al. 2005). Samples obtained inside and outside a residential house in Al-Suwayq (Oman) contained quartz, dolomite, and gypsum. Calcite, quartz, dolomite, and goethite were detected in samples obtained in a residential house near a cement plant.

Settled dust collected from five family farms located in Lublin, Jastków, Konopnica, and Niemce, Poland contained 0.7–65.2% silica (Molocznik 2002). Average free silica content in bituminous coal was 174,000 ppm (standard deviation 94,000) from Xuan Wei, China and 18,000 ppm (standard deviation 17,000) from the United States (Large et al. 2009). Grainsize analysis of coal from Xuan Wei, China indicates that 35–55% of the total quartz had a particle size <10 µm.

Ash from the Eyjafjallajökull Volcano eruption in 2010 and from the eruption of Grímsvötn, Iceland in 2011 was studied and compared to ash from Soufrière Hills Volcano, Montserrat that has been studied since eruptive activity began in 1995 (Horwell et al. 2013). Ash from Eyjafjallajökull had a c-silica abundance of 1.4–3.2 weight % and ash from Grímsvötn did not have detectable c-silica content. Ash samples from Soufrière Hills contained 5.2–15.2 weight % cristobalite and 1.2–1.6 weight % quartz (Horwell et al. 2010). c-Silica is formed in volcanic environments by lava dome eruptions with viscous, silicic magma extruded from the volcano at approximately 800°C, forming a dome of rock in the crater (Horwell et al. 2012).

Amorphous Silica. According to the European Centre for Ecotoxicology and Toxicology of Chemicals Joint Assessment of Commodity Chemicals report (ECETOC 2006), a-silica levels in soil and sediment were approximately 706 and 524 g/kg (dry weight). In the Seine River watershed, mean a-silica mean concentrations were 5.2, 4.7, and 3.9 mg Si/g in cultivated soil, meadow, and forest, respectively. Suspended matter from the winter and summer had a-silica average concentrations of 5.7±0.9 and 18.4 mg Si/g (Sferratore et al. 2006).

5.5.4 Other Media

Organisms, such as diatoms and radiolarian, build up exoskeletons of hydrated a-silica from silicic acid in water. Plants use silicic acid to make a-silica materials for strengthened stems and leaves or protective spikes (Ning 2002). a-Silica also accumulates in rice, millet, sugarcane, and wheat plants (Rabovsky 1995). Liu et al. (1996a) measured free silica content of rice husk ash to be 91.4% (25.5% cristobalite and 3.6% tridymite) when the rice husk was burned at 1,100°C; however, the silica content was dependent on the temperature of burning. When the rice husk was burned at 350°C, the ash contained 23% free silica, of which 1.1% was quartz, 3.4% was cristobalite, and 0.5% was tridymite. Tridymite is rarely reported in the workplace or found in nature (Smith 1998).

Le Blond et al. (2010) reported raw air dried sugarcane leaf silica concentrations ranging between 0.45 and 1.8 weight %. Sugarcane trash ash burned at temperatures up to 1,056°C had silica concentrations ranging from 10.38 to 24.77 weight %. Bagasse, the fibrous remains left after sucrose extraction, is often burned as an energy source. The bagasse ash contained between 39.2 and 40.0 weight % silica content. No c-silica was found in the ash burned at temperatures <800°C; however, cristobalite and quartz formed when the sugarcane burned at higher temperatures.

High-purity, mesoporous a-silica was found in a study of the freshwater sponge, *Cauxi*. The study evaluated the skeleton and spicules of a sample made of glassy silica with a length of 305±18 and a width of 15.6±1.5 μm (Jensen et al. 2009). An axial filament that is known to contain the silica catalyst protein, silicatein α, was also evaluated.

5.6 GENERAL POPULATION EXPOSURE

Crystalline Silica. c-Silica is ubiquitous in the environment. Over 95% of the earth's crust is made of silica-containing minerals and c-silica (Uhrlandt 2006). As silica is part of the natural environment and widely distributed in soils and rocks, predominantly as quartz, exposure to c-silica is unavoidable (IARC 1997). c-Silica exposure is expected in both occupational and general settings from the natural environment and consumer use of products containing c-silica (NTP 2014; USGS 1992). It is important to consider the form and availability of silica when discussing silica exposure because silica has multiple forms, particle sizes, surface areas, and surface chemistry (OSHA 2013c). Inhalation is expected to be the primary route of exposure to c-silica for the general population from the use of commercial products containing quartz (IARC 2012). Occupational exposure to c-silica is further discussed in Section 5.7, Populations with Potentially High Exposures.

c-Silica is an established air contaminant. Local meteorological conditions can give rise to silica-containing dust, most notably in areas around recent volcanic eruptions, mine dumps, and deserts (e.g., sand storms) (IARC 1987, 1997). People who live near quarries, sand or gravel operations, or hydraulic fracturing operations may be exposed to respirable c-silica. Consumer exposure to respirable c-silica is possible from the use of abrasives, sand paper, detergent, grouts, and concrete (IARC 1997). Diatomaceous earth is used as a filler in reconstituted tobacco sheets and may be converted to cristobalite at high temperatures when passing through the burning tip of tobacco products (IARC 1987).

Dermal and oral exposure to quartz may occur through the use of consumer and commercial products, including cleansers, skin care products and soaps, art clays and glazes, pet litter, talcum powder, caulk, pharmaceuticals, putty, paint, and mortar (NTP 2009). A homeopathic remedy called silicea, prepared from flint, quartz, sandstone, and other rocks, is another potential source of dermal silica exposure. Although quantitative data are not available, ingestion of potable water containing quartz particles is a potential source of exposure for the general population (IARC 2012).

Amorphous Silica. As with c-silica, a-silica is widespread in nature. Biogenic forms are found in diatomaceous earth and various plant life, particularly grasses, which release a-silica into the soil through burning or normal decay. Non-biogenic forms are found in volcanic glass (IARC 1997).

Inhalation is the primary source of concern for occupational exposure to a-silica. Diatomaceous earth miners and sugarcane and rice farmers may be exposed to natural sources of a-silica. Workers involved in ferrosilicon industrial processes and workers that produce or use synthetic a-silica products may also be exposed (IARC 1997). Occupational exposure to a-silica is further discussed in Section 5.7, Populations with Potentially High Exposures.

People who live near power stations and various silicon manufacturing facilities may be exposed to a-silica (and c-silica) via fly ash release. Additionally, people living near sugarcane and rice farms may be exposed to elevated air levels of biogenic a-silica fibers (IARC 1997).

Exposure to a-silica may occur through dietary intake based on the widespread use of synthetic a-silica compounds in the food, cosmetics, and pharmaceutical industries as anticaking agents or carriers. Specifically, synthetic a-silica used in food packaging is expected to be an important source of exposure (FDA 2015a, 2015b). The potential for migration into food will depend on the degree to which it is encapsulated into the packaging matrix (Bott et al. 2015; Stormer et al. 2017). The average daily intake of a-silica from food ranges from 0.28 to 12.7 mg/kg/day, with dietary supplements delivering doses up to 700 mg/day (Fruijtier-Polloth 2016). According to the European Centre for Ecotoxicology and Toxicology of Chemicals Joint Assessment of Commodity Chemicals report (ECETOC 2006), U.S. drinking water contains a median dissolved silica concentration of 7.1 mg/L. In the Seine River watershed, the average a-silica concentration in tap water and two water treatment plants was 4.1 mg/L (Sferratore et al. 2006). Although quantitative data are not available, diatomite fragments are present in drinking water worldwide, and are a potential source of exposure for the general population (IARC 1997).

Exposure to a-silica may occur through use of silicon dioxide (diatomaceous earth) and silica gel pesticides to control insects and arachnids in stored grain crops, food handling areas, hospitals, and sewage systems; on animals/pets; or in living quarters (EPA 1991).

Dermal exposure to a-silica may occur through contact with use of consumer and commercial products, including cosmetics (e.g., makeup, hair products, toothpaste, personal cleanliness and bath products, skin care products, underarm deodorants, perfumes, foot powders and sprays), paints and adhesives, and silica gel pesticide products (EPA 1991; Florke et al. 2008; Fruijtier-Polloth 2016; Merget et al. 2002).

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Occupational Exposure to Crystalline Silica. Respirable c-silica is extremely common, is widely used in materials and products, and is naturally occurring; therefore, occupational exposures occur in a variety of industries and occupations (NIOSH 2002). Metal, nonmetal, and coal mines and mills, granite quarrying and processing sites, hydraulic fracturing operations, crushed-stone industries, foundries, ceramics, construction, and sandblasting operations are most frequently found to have respirable quartz levels >0.1 mg/m^3 (NTP 2014). Main industries where c-silica exposure is likely are those that require job activities involving the movement of earth, disturbing products containing silica, and handling or use of sand and other silica-containing products (IARC 1997, 2012). Workers in other industries also have reported exposure to silica, including shipbuilding and repair, rubber and plastics, paint, soap and cosmetics, roofing asphalt and felt, agricultural chemicals, jewelry, arts, crafts, sculpture, counter manufacture and installation, dental material, boiler scaling, and automobile repair (NIOSH 2002).

A total of 81,221 workers had the potential to be exposed to quartz at 4,077 facilities in 59 industries in 1972–1974 based on data from a National Occupational Hazard Survey conducted from 1972 to 1974 (NTP 2014). The survey for 1981–1983 reported that 944,731 workers (112,888 women) were potentially exposed to quartz and 31,369 workers (2,228 were women) were potentially exposed to cristobalite (NTP 2014). NIOSH estimated that approximately 1.7 million workers had the potential to be exposed to respirable c-silica based on data from 1986, of which 722,708 workers were in mining industries and 522,748 workers were in non-mining industries (NIOSH 2002).

Yassin et al. (2005) estimated that 119,381 workers in the United States are potentially exposed to high levels of c-silica based on data from 7,209 personal sample measurements collected from 1988 to 2003 stored in the OSHA Integrated Management Information System (IMIS) database. Geometric mean airborne silica exposure levels among workers were 0.070 mg/m^3 from 1988 to 1991, 0.068 mg/m^3 from 1992 to 1995, 0.080 mg/m^3 from 1996 to 1999, and 0.073 mg/m^3 from 2000 to 2003. Freeman and Grossman (1995) evaluated data for measured respirable quartz in 1,655 inspections from 255 industries collected by OSHA. The most severe 8-hour TWA exposures were in the fabricated structural metal and painting and paper hanging industries.

Radnoff et al. (2014) evaluated the occupational exposure of workers in Alberta, Canada to respirable quartz. Workers in the oil and gas industry had the highest maximum exposure of 8.6 mg/m^3; however, workers in the sand and mineral processing industry had the highest geometric mean exposure to quartz at 0.09 mg/m^3. Bricklayer and concrete job activities (coring, cutting, or finishing) had a geometric mean exposure concentration of 0.105 mg/m^3 respirable quartz exposure, which was the highest among the occupations in the study. In Italy, geometric mean occupational exposure to respirable c-silica concentrations ranged from 0.007 mg/m^3 for workers in the manufacture of basic metals to 0.045 mg/m^3 for construction workers (Scarselli et al. 2014).

Agricultural workers in the United States may be exposed to dust containing a significant percentage of respirable c-silica (Linch et al. 1998). In agriculture operations, plowing, harvesting, using machinery, burning agricultural waste, and processing agricultural products are possible routes of silica exposure from the soil (NIOSH 2002). Farmers may be exposed to cristobalite (and a-silica) during crop burning or incineration (Rabovsky 1995). Agricultural workers from 10 farms in Yolo and Solano counties in California wore personal sampling equipment to measure exposure to inhalable and respirable dust levels (Nieuwenhuijsen et al. 1999). The geometric mean concentration of respirable dust ranged from 0.05 to 2.83 mg/m^3 (the dust contained 18.6% c-silica). Inhalable dust concentrations ranged from 0.30 to 45.14 mg/m^3 and contained 7.4% c-silica overall. Respirable silica concentrations were measured for farm workers in eastern North Carolina (Archer et al. 2002). The mean silica concentrations ranged from below the level of detection (0.005 mg/m^3 quartz) to 3.91±2.31 mg/m^3 for sweet potato planting in Wayne County.

Respirable quartz concentrations were measured at three South African farms with either sandy, sandy loam, or clay soil (Swanepoel et al. 2011). The geometric mean respirable quartz concentrations were 0.0317, 0.0316, and 0.031 mg/m^3 for the sandy soil, sandy loam soil, and clay soil farms, respectively. The level of silica in air collected from five family farms located in Lublin, Jastków, Konopnica, and Niemce, Poland contained 1.1–22% silica (Molocznik 2002).

Industrial hygiene practices such as engineering controls, tailored work practices, respirators, and worker training can be used to minimize potential silica health hazards. In the construction industry, wet cutting using water to control airborne dust levels and vacuum dust collection are used to reduce silica dust exposure (OSHA 2009). Construction workers may become exposed to silica from sand, concrete, rock, soil, mortar, plaster, and shingles (NIOSH 2002). In ‘new’ construction, concentrations of respirable c-silica range from 0.013 to 1 mg/m^3 (Radnoff et al. 2014). In the United States, a study evaluated silica exposure at 36 construction sites (Rappaport et al. 2003). The highest exposures, with a median silica concentration of 1.28 mg/m^3, were from painters, followed by laborers at 0.350 mg/m^3, bricklayers at 0.320 mg/m^3, and operating engineers at 0.075 mg/m^3. Quartz dust geometric mean concentrations ranged from 0.01 mg/m^3 (geometric standard deviation of 2.6) to 0.61 mg/m^3 (geometric standard deviation of 5.4) for the tuck point grinder job in a personal silica exposure monitoring data study of the construction industry (Flanagan et al. 2006).

Abrasive blasting is considered to be one of the more hazardous operations involving silica, and it is important for workers performing this task to use proper respiratory protection (Madl et al. 2008). A study was performed to evaluate 11,845 measurements obtained for exposure to respirable c-silica in the construction industry (Beaudry et al. 2013). The majority of the measurements (92%) were obtained with personal measurement devices from 1974 to 2009. The highest geometric mean concentration of c-silica that workers were exposed to was 1.59 mg/m^3 for the abrasive blasting task. In New Jersey, occupational exposure monitoring was performed for a footbridge repainting project using a substitute abrasive with no to low abrasive content in 2002 (Meeker et al. 2005). The workers' exposures to respirable silica were still high, most likely because a high level of silica contaminant, ranging from 0.52 to 25.66 mg/m^3, was found in the surface paint. Personal samples for exposure to quartz were collected on heavy and highway construction workers (Woskie et al. 2002). The geometric mean concentration for respirable quartz ranged from 0.007 to 0.026 mg/m^3 for the job tasks of operating engineers and laborers, respectively. Personal breathing zone air samples were collected to analyze home construction roof workers' exposure to c-silica (Hall et al. 2013). The 8-hour respirable dust concentration ranged from 0.2 to 3.6 mg/m^3. The respirable silica 8-hour exposures ranged from 0.04 to 0.44 mg/m^3. The geometric mean concentrations of respirable silica were 0.12, 0.14, 0.16, and 0.14 mg/m^3 for four companies.

Granite and marble countertop workers had 8-hour TWA exposures as high as 3.07 mg/m^3 (14% quartz) in a 1999 OSHA inspection and 7.4 mg/m^3 (0.7% quartz) based on personal monitoring data (Fairfax and Oberbeck 2008). Akbar-Khanzadeh et al. (2007) measured the concentration of c-silica dust and respirable particulate matter encountered during indoor concrete grinding, wet grinding, and ventilated grinding and uncontrolled conventional grinding. The mean TWA c-silica dust concentrations with no general ventilation were 86.0 mg/m^3 for uncontrolled grinding, 1.40 mg/m^3 for wet grinding, and 0.161 mg/m^3 for local exhaust ventilation grinding; when general ventilation was used, the dust concentrations were 25.4 mg/m^3 for uncontrolled grinding, 0.521 mg/m^3 for wet grinding, and 0.148 mg/m^3 for local exhaust ventilation grinding. c-Silica dust mean concentrations during surface concrete grinding with a 100–125 mm grinding cup were 0.17 and 0.11 mg/m^3 with a HEPA-cyclone and HEPA tank, 0.54 and 0.12 mg/m^3 with a shop vacuum, 0.96 and 0.27 mg/m^3 with wet grinding, and 23.6 and 5.78 mg/m^3 with and without general ventilation, respectively (Akbar-Khanzadeh 2010). When a 180-mm cup was used, the silica dust concentrations were 0.54 and 0.20 mg/m^3 with a HEPA-cyclone and HEPA tank, 1.90 and 0.14 mg/m^3 with a shop vacuum, 8.83 and 2.08 mg/m^3 with wet grinding, and 55.3 and 15.1 mg/m^3 with and without general ventilation, respectively.

The mean exposure to respirable dust and quartz was reported for the Dutch construction industry (van Deurssen et al. 2014). The overall mean concentrations were 0.88 mg/m^3 for respirable dust and 0.10 mg/m^3 for quartz. The concentrations ranged from 0.02 to 33.76 mg/m^3 for respirable dust and from 0.01 to 1.36 mg/m^3 for quartz.

Workers in the nonmetal mining operations (i.e., sandstone, clay, shale, and miscellaneous nonmetallic mineral mills) had higher exposure to silica dust than those in metal mining operations. Baggers, general laborers, and personnel involved in the crushing, grinding, and sizing operations had the highest exposure within the mills (IARC 1987). In samples obtained from metal and nonmetal mines from 2005 to 2010, the respirable dust geometric mean concentrations were highest in underground nonmetal and limestone mining samples at 0.88 and 0.73 mg/m^3, with quartz present in 0.029 and 0.024 mg/m^3, respectively (Watts et al. 2012). The highest geometric mean quartz concentration was found in underground sand and gravel mines at 0.068 mg/m^3.

In a cohort mortality study of North American industrial sand workers, the overall geometric mean exposure to respirable c-silica was calculated to be 0.042 mg/m^3 based on 14,249 measurements taken between 1974 and 1998 (Rando et al. 2001). Granite shed workers in Elberton, Georgia were exposed to respirable c-silica at a mean exposure concentration of 0.052 mg/m^3 (Wickman and Middendorf 2002). Exposure surveys were conducted in a granite quarry with side-by-side arrays of four closed-face cassettes, four cyclones, four personal environmental monitors, and a real-time particle counter (Sirianni et al. 2008). c-Silica concentrations ranged from 0.41 mg/m^3 from a personal exposure monitor to 12.38 mg/m^3 for a closed-face cassette. Differences were reported related to the size and silica content of airborne particles depending on the tools being used and the granite activity level at the time of sampling.

In a c-silica occupational exposure study performed in the United States, a geometric mean of 0.065 mg/m^3 was reported for all occupations in the stonework masonry industry based on data collected between 1988 and 2003 (Yassin et al. 2005). A study evaluating the occupational exposure for workers at 18 silica sand plants from 1974 to 1996 from 4,269 respirable dust samples, reported a geometric mean quartz concentration of 25.9 mg/m^3 (geometric standard deviation of 10.9), and samples ranged from <1 to 11,700 mg/m^3 (Sanderson 2000).

An average concentration of 0.22 mg/m^3 was reported for 148 carvers at a stone-carving company in Thailand (Yingratanasuk et al. 2002). Pestle makers and mortar makers had exposure to c-silica at concentrations of 0.05 and 0.88 mg/m^3, respectively. Personal sampling by workers in a small-scale mining operation reported 15.5 mg/m^3 respirable dust, 2.4 mg/m^3 respirable c-silica, 1.5 mg/m^3 respirable combustible dust, and 28.4 mg/m^3 ‘total’ dust during activities such as drilling, blasting, and shoveling (Bratveit et al. 2003). Respirable dust and respirable c-silica were 4.3 and 1.1 mg/m^3, respectively, during shoveling and loading of sacks. An overall geometric mean of 0.09 mg/m^3 of respirable c-silica was reported from samples collected at seven U.K. quarries between 1978 and 2000 (Brown and Rushton 2005a).

Occupational exposure of coal miners to respirable coal mine dust in the United States was evaluated using data collected from 1995 to 2008 (Joy 2012). Quartz content in airborne dust was variable, and >5% quartz content was found in 20,193 samples (21.6%) below the 0.100 mg/m^3 respirable dust standard. Average respirable quartz exposure concentrations for miners at surface coal mines in the United States ranged from 0.08 mg/m^3 in 1986 to 0.15 mg/m^3 in 1982 based on data from the Mine Safety and Health Administration (MSHA) inspectors (Piacitelli et al. 1990).

Average exposure was calculated using MSHA compliance data from 16,578 measurements at 4,726 mines obtained from 1998 to 2002 (Weeks and Rose 2006). Continuous miner operators were exposed to a mean concentration range of 0.0061–0.2717 mg/m^3. Workers in underground mines had the highest geometric mean concentration of 0.050 mg/m^3. Workers in strip and open pit mines and mills or preparation plants had slightly lower mean concentrations of 0.047 and 0.045 mg/m^3, respectively.

The overall geometric mean concentration of respirable c-silica was 0.027 mg/m^3 for underground coal mining in the United Republic of Tanzania (Mamuya et al. 2006). Employees for the development team, mine team, transport team, and maintenance team reported geometric mean concentrations of 0.073, 0.013, 0.006, and 0.016 mg/m^3, respectively. A study evaluating respirable samples for silica exposure from two copper mines in Mufulira and Nkana, Zambia reported concentrations of 0.143±0.2 and 0.060±0.06 mg/m^3 of respirable quartz, respectively (Hayumbu 2008). The mean respirable quartz concentration reported in Ontario gold mines ranged from 0.02 mg/m^3 for the task operations designated as other to 0.17 mg/m^3 for the conveying and transporting operations (Verma et al. 2014). The highest (or maximum) concentration reported was 0.85 mg/m^3 for the Conveying and Transporting task.

Personal respirable dust exposures were collected at crushed stone facilities in the United States (Kullman et al. 1995). Workers with limestone were exposed to dust with an 11% mean α-quartz content or a geometric mean concentration of 0.04 mg/m^3 (standard deviation 1.88). Workers with granite were exposed to dust with 37% mean α-quartz content or a geometric mean concentration of 0.06 mg/m^3 (standard deviation 1.94). Workers with Traprock were exposed to dust with 15% mean α-quartz content or a geometric mean concentration of 0.04 mg/m^3 (standard deviation 1.62). Silica flour is made by drying and milling mined quartz into fine particles, many of which are respirable (MMWR 1989). The MSHA measured respirable quartz exposures at 28 plants using personal breathing-zone air samplers and found free silica levels above the MSHA permissible exposure limit (PEL) of 0.1 mg/m^3 in 52% of the samples.

Exposure levels to airborne respirable dust with quartz powder sizes of 1.52–3.04 or 3.04–6.08 mm in quartz manufacturing units in India were studied (Fulekar 1999). The mean respirable dust exposure level was 2.93 mg/m^3 and exposures ranged from 0.11 to 11.2 mg/m^3 with a high silica content, ranging from 86 to 98%. The TWA exposure of stone crushing laborers in India for PM$_{2.5}$ c-silica was 2.29 mg/m^3 (Semple et al. 2008). Occupational exposure to silica was evaluated at slate pencil manufacturing units in India (Fulekar and Khan 1995). Total and respirable dust was present at concentrations up to 380.50 and 31.44 mg/m^3, respectively, based on data from the study performed in 1977. Total and respirable dust was present at concentrations as low as 4.04 and 0.61 mg/m^3, respectively, in a study performed in 1991. The free silica content was 35–40, 42–47, and 35–47% in three studies performed in 1977, 1982, and 1991 respectively.

Quartz exposure levels were measured in the Alta, Northern Norway slate industry (Bang and Suhr 1998). The slate factory had respirable quartz average concentrations of 0.12 mg/m^3 inside and 0.13 mg/m^3 outside. c-Silica exposure was measured in the Norwegian silicon carbide industry using 720 fiber samples, 720 respirable dust samples, and 1,400 total dust samples (Foreland et al. 2008). Respirable cristobalite geometric mean levels ranged from below the limit of detection to 0.038 mg/m^3 (geometric standard deviation of 2.0). Respirable quartz geometric mean levels ranged from below the limit of detection to 0.020 mg/m^3 (geometric standard deviation of 2.1). Personal airborne geometric mean concentrations of quartz and cristobalite were 0.013 mg/m^3 (geometric standard deviation of 4.58) and 0.010 mg/m^3 (geometric standard deviation of 2.10) for workers performing the carboselector job (Dion et al. 2005). The workers with the job title, Attendant in Acheson furnace maintenance, had a geometric mean quartz exposure of 0.079 mg/m^3 (geometric standard deviation of 1.49).

During the hydraulic fracturing process, large quantities of silica sand, with up to 99% silica, are used for pumping into wells at high pressure (Chalupka 2012). Data from 111 personal breathing zone samples at 11 sites in five states were evaluated by NIOSH to determine worker exposures to respirable c-silica during hydraulic fracturing (Esswein et al. 2013). The median percentage of quartz in 111 personal breathing zone samples was 53%. Total geometric mean concentrations of respirable quartz were 0.122 mg/m^3 for all samples and the geometric standard deviation was 1.152. Workers with the job titles, T-belt Operator and Sand Mover Operator, had the highest geometric mean concentrations of respirable c-silica of 0.327 and 0.259 mg/m^3, respectively, compared to other job titles.

Operations in the ceramic, brick, and clay industries result in c-silica emissions through kiln drying of clay and brick objects, crystalline sand processing, glass manufacturing, calcining of diatomaceous earth, and pottery manufacturing (EPA 1996). Birk et al. (2010) evaluated respirable c-silica measurements obtained from 1955 to 2006 for worker exposure in the ceramics industry. Typically, the highest exposure occurred in the historic samples obtained in 1955–1959 for all job task activities. The highest exposure geometric mean concentration of respirable c-silica in the 2000–2006 data set was from the preparation task at 0.03 mg/m^3. A heavy clay industry exposure study was performed with 18 factories from England and Scotland and 1,400 personal dust samples (Love et al. 1999). Mean quartz concentrations ranged from 0.04 to 0.62 mg/m^3 for non-process workers and kiln demolition workers, respectively. Respirable α-quartz concentrations were measured for workers in the refractory material manufacturing industries (Chen et al. 2007). A minimum variance unbiased estimate of the arithmetic mean respirable α-quartz content ranged from 0.0298 mg/m^3 in the crushing area to 0.0681 mg/m^3 in the mixing area.

OSHA sampling on the melt deck and sprue line of a ductile and malleable iron foundry detected c-silica at 0.21 mg/m^3 based on the TWA; however, employees engaged in the furnace cleaning and scrapping were exposed to 7.92 and 0.54 mg/m^3, respectively (Strelec 2010). Personal monitors were used to collect 158 measurements of respirable quartz from jobs conducted from 1993 to 1998 (Maxim et al. 1999). Most of the respirable c-silica concentrations, 91.14%, were less than the limit of detection; the remainder ranged from 0.010 to 0.100 mg/m^3. Occupational silica exposures were evaluated for workers at a grey and ductile iron foundry that manufactures heavy industrial castings, such as transmission housings for large trucks (Lee 2009). The 8-hour TWA c-silica concentrations ranged from 0.988 mg/m^3 for a molder to 4.38 mg/m^3 for a grinder based on the results obtained from personal sampling devices.

Andersson et al. (2012) performed an exposure assessment of quartz in Swedish iron foundries using both historical and current data. The job title with the highest mean quartz exposure was the furnace and ladle repair, with a total concentration of 0.42 mg/m^3, and the lowest was the core maker, with a total concentration of 0.024 mg/m^3. The arithmetic mean minimum variance unbiased estimate of respirable quartz exposure profiles for workers during a municipal waste incinerator relining ranged from 0.040 to 0.578 mg/m^3 (Shih et al. 2008). In Khaf, Iran, occupational exposure to respirable quartz was evaluated for workers at an iron ore mine (Naghizadeh et al. 2011). The maximum mean concentration of total quartz was at the crusher machine station at 26 mg/m^3 with a standard deviation of 7, and the minimum concentration was 0.012 mg/m^3 with a standard deviation of 0.002.

At a flat outdoor firing range in 2004, quartz levels were found to exceed 0.030 mg/m^3 (Mancuso et al. 2008); the likely source of the quartz was the sand on the floor of the range. In 2006, after the sand was changed, barrier curtains were added, and lava rock was added to the floor for silica exposure control, the quartz levels were below 0.018 mg/m^3. At a tunnel type outdoor firing range, personal sampling devices found quartz silica levels ranging from 0.15 to 0.21 mg/m^3. After Hurricane Sandy in 2012, clean-up workers were monitored for silica exposure (Freund et al. 2014). One measurement of 0.015 mg/m^3 taken at Rockaway, New York in the vicinity of sand was above the detection limit.

Diatomaceous earth mining, processing, and production reported respirable dust levels ranging from 0.1 to 28.2 mg/m^3 with a c-silica content ranging from <1 to 75% (IARC 1997). Diatomaceous earth workers have the potential for inhalation exposure to high levels of respirable cristobalite and quartz that may be present as impurities or from heating silica (IARC 1997; Rabovsky 1995). In industries where silica products are heated, such as refractory brick and diatomaceous earth plants and ceramic and pottery manufacturing plants, occupational exposure to cristobalite may occur (IARC 1997).

At a diatomaceous earth mining and milling facility in California, respirable c-silica average cumulative exposure was 0.29 mg/m^3 per years of employment. The c-silica content of the diatomaceous earth dusts varied from 1 to 25% from 1942 to 1994 (Park et al. 2002). Final cumulative exposures to total respirable dust and respirable c-silica dust were 7.31 mg/m^3·years (average; 168.84 maximum) and 2.16 mg/m^3·years (average; 62.52 maximum), respectively (Checkoway et al. 1997).

Occupational Exposure to Amorphous Silica. Occupational exposure to a-silica may occur in the use or manufacture of a-silica and a-silica-containing products, such as synthetic resins, plastics, lacquers, vinyl coatings, varnishes, pharmaceuticals, cosmetics, adhesives, paints, and foods (IARC 1997). Workers in other industries, such as glass, ceramics, cement, refractory brick, paper, paint, and rubber, may be exposed to various forms of a-silica when used as fillers, filters, or other purposes (NIOSH 2002). In an occupational exposure study, 1,375 inhalable synthetic a-silica dust concentration measurements were performed from five German synthetic a-silica plants producing pyrogenic and precipitated forms of silica (Morfeld et al. 2014). Mean aerodynamic diameters of the a-silica were 200 µm. Exposures were grouped into categories of low (<1 mg/m^3), medium (1–4 mg/m^3), high (4–10 mg/m^3), and peak (>10 mg/m^3). Using two different exposure estimate procedures, cumulative exposure estimates averaged 56.9 mg/m^3-years (expert assessment) and 31.8 mg/m^3-years (multiple exposure assessment). Older studies in plants that use or produce synthetic a-silica have also reported dust concentrations ranging from 0 to 10 mg/m^3 (IARC 1997).

Diatomaceous earth miners can be exposed to natural a-silica dust during extraction, with measured respirable dust concentrations ranging from 0.1 to 28.2 mg/m^3; however, most studies are more focused on potential c-silica exposure, which ranges from <1 to 75% of respirable dust, depending upon how the diatomaceous earth is processed (IARC 1997).

Sugarcane farmers may be exposed to biogenic a-silica fibers, particularly during harvesting, cutting, and milling at concentrations ranging from 6,200 to 300,000 fibers/m^3 (IARC 1997). It should be noted that sugarcane workers are also expected to be exposed to c-silica during the harvesting process when sugarcane plants are burned (Le Blond et al. 2010). Low levels of biogenic a-silica fibers have also been reported during field preparation, harvesting, and transport of rice crops, at concentrations ranging from 0.13 to 1 fiber/mL (IARC 1997).

a-Silica fume is a byproduct of the ferrosilicon industrial process (IARC 1997). Total dust containing synthetic-precipitated a-silica was measured at three chemical plants at concentrations of 0–10.5 mg/m^3. Total dust and respirable dust from personal samples obtained from synthetic pyrogenic fumed manufacturing plants was found at median concentrations of 0.61–6.5 and 0.2–2.1 mg/m^3, respectively. One ferrosilicon industry exposure study reported 22.3% silica content (amorphous and crystalline) in total dust found at concentrations of 7.3 mg/m^3. In another ferrosilicon industry exposure study, maintenance workers had respirable dust containing a-silica exposures ranging from 0.27 to 2.24 mg/m^3.

Exposures in Children. Exposure of children to c- and a-silica from breathing air, drinking water, and eating food is expected. As both c- and a-silica are part of the natural environment and found widely in soils, rocks, water, and foods, exposure to silica is unavoidable. Children are likely to ingest dirt from their unwashed hands or when playing with soils, and may be exposed to silica in this manner. Children living in proximity to mines, quarry sites, or industries that release silica particulates to the environment may be exposed to higher levels of silica than are found in the natural environment via inhalation of silica from dust that is entrained in air. Silica is a major component of sand and dirt and may be in many forms; some of these forms may be embedded in minerals.

Dermal and oral exposure may occur through the use of consumer and commercial products that contain silica, including cleansers, skin care products and soaps, art clays and glazes, talcum powder, and pharmaceuticals (NTP 2009). Both silicon dioxide and diatomaceous earth may be found in food and are listed on the Everything Added to Food in the United States (EAFUS) report of items added directly to food that the FDA has either approved as food additives or listed or affirmed as Generally Recognized As Safe (GRAS) (FDA 2013). However, average daily intakes and exposure information for children were not available.