Introduction - Natural Beryllium in the Environment

Beryllium is a naturally occurring element (atomic number 4) and is one of the lightest of elements with an atomic weight of 9.012. Beryllium enters the air, water and soil as a result of natural and human-related activities. Beryllium is ubiquitous in nature, typically occurring as a mineral silicate. It is the 44th most abundant element in the earth's crust. Beryllium is typically found at levels of 0.5 to 2 ppm in soils and rocks throughout the world. Extracted pure beryllium (Be) is a hard, grayish-white metal of the alkaline earth family. Beryllium does not occur naturally in its pure form. Because beryllium occurs in trace quantities in all soil and rock, as a result of weathering, it releases as a particulate compound to air, water and sediments. Due to uptake from soil, plants and foodstuffs commonly contain parts per billion concentrations of beryllium.

The only minerals mined for purposes of extracting beryllium metal are bertrandite (0.5 – 1.0% Be) and beryl ores (0.5 – 3.5% Be). The gemstone Emerald is a beryl mineral.

Commonly used clay and mineral-based materials containing trace quantities of beryllium are used to make products for use in manufacturing, construction and consumer products. The existence of beryllium in these materials is coincidental: these materials are not used because of the trace amounts of beryllium. Common examples include oil-dry, oil, emery cloth, grinding wheels, coal, abrasive blast media, concrete, bricks, roofing shingles, kitty litter, charcoal, laundry detergent and ceiling tiles. These materials contain beryllium at concentrations typically found in soils.

The use of clay and mineral-based materials containing trace quantities of naturally occurring beryllium in manufacturing can result in worker exposures in excess of the EU 8-hour occupational exposure limit for beryllium in very dusty operations. It is important to understand that beryllium-related disease has not been found with certainty in studies of workers exposed to trace beryllium originating from natural materials or from processing materials where beryllium has not been intentionally added for its unique properties. Only materials and products where beryllium has been intentionally added for its unique properties have been found to pose a beryllium health risk.

Beryllium in Soil and Rock

The concentrations of beryllium in soil typically range from 0.5 - 2.0ppm (mg/kg). Beryllium in soil primarily results from erosion of rock and deposition from volcanic activity and the combustion of fossil fuels. Examples of concentrations in soils and sediments include:

- 0.6 – 15 ppm in earth's crust (EPA 1987 & Chiasson 1991)
- Mean 0.9ppm in soils (U.S. Geological Survey #1270)
- Japan 0.9 -1.9 ppm in soil (Fukazawa 1984)

The sedimentary cycle begins when the parent rock is broken down by weathering (physical, chemical, or biological). Weathering is the first phase of the sedimentary cycle and is responsible for eroding and fracturing rocks and liberating rock particles. Once liberated, small rock particles left by weathering are available for movement within the environment via natural transport forces such as wind, rain, and snow. (Mason & Dragun 1996)

Weathering effects cause erosion or disintegration of beryllium-bearing minerals by mechanisms similar to other types of rocks. In the case of beryllium-bearing minerals, beryllium is typically locked within a silicate matrix. Degradation of the ore body by weathering exposes the individual beryllium minerals but does not liberate beryllium as a soluble species because the mineral structure remains intact.

There are some forty-odd recognized mineral forms of beryllium. These known beryllium-containing minerals usually occur in pegmatites, in granites, in syentites, and occasionally in gneisses and mica sheets. At present, only beryl and bertrandite ores are mined commercially.

Though beryllium is a naturally occurring element, human related processes i.e., the combustion of fossil fuels, can contribute to the levels found in soil at the earth's surface. The distribution of beryllium in soil can be affected by weather patterns around combustion sources. The United States Department of Energy conducted a large soil survey in the U.S. The National Uranium Resource Evaluation (NURE) / Hydrochemical and Stream Study Reconnaissance (HSSR) study began in 1974. The program analyzed for 70 elements sampled from 320 quadrangles in 33 states and was completed in 1980. The study included over 200,000 samples for beryllium. In this dataset, small differences in concentrations of beryllium in soil could be seen downwind of large combustion sources. The following are the overall soil and sediment sample results from the study:

NURE Soil samples

Maximum Be - 1312.0 ppm
Mean (average) Be - 1.8 ppm

NURE Sediment samples

Maximum Be - 731ppm
Mean (average) Be - 1.5 ppm

Beryllium in soil does not dissolve in water but remains bound to the soil. Once in the soil, the beryllium is not very likely to move deeper into the ground and enter groundwater. USEPA

Beryllium in Water

Minerals containing beryllium occur naturally in ground water and surface water. Beryllium contained as mineral chemical compounds are largely water insoluble, have a low aqueous solubility, and are carried in suspension within the environment. Particles carried in suspension are much more influenced by turbulence and velocity effects. Such particles will be carried in suspension as long as the water velocity remains constant. In deeper areas, where the water pools, or areas along the outer edge where the water slows down, particle sedimentation or drop out usually begins. (Mason & Dragun 1996)

Beryllium has been measured in ground water in the United States at an average concentration of 13.6 µg/l (ppb) and in surface water at an average concentration of 23.8 µg/l (ppb). Drinking water data reported from the Czech Republic (F. Kozicek 2009) found average beryllium

concentration in 19173 water samples taken in 2004–2008 was 0.19 µg/l, with a median of 0.1 µg/l. In 11.29% of samples, the concentration was below the limit of determination, whereas the concentrations of 101 samples (0.53%) were above 2 µg/l, with a maximum of 35 µg/l.

The U.S. ATSDR reports beryllium in drinking water to range from 0.010 to 1.22 µg/l with an average of 0.19 µg/l. Beryllium was not found in 95% of 1,577 drinking water samples obtained throughout the United States (Trace Elements in the Environment U.S. Department of Commerce PB-274-428). An Australian survey found 0.08 µg/l beryllium in rainwater. The concentration of total beryllium in ocean water ranges from 0.02 to 0.9 Ng/L, with an average of <0.5 Ng/L (Measures and Edmond 1986; Merrill 1960).

Mineral bound beryllium enters waterways from the erosion of rocks and soil, with most of the beryllium settling in bottom sediments. According to WHO, in most natural waters, the majority of beryllium minerals are adsorbed to suspended matter or in sediment, rather than dissolved. does not dissolve in water but remains as a bound mineral in the soil. Beryllium in sediment is primarily adsorbed to clay. For example, in the Great Lakes in the U.S., beryllium is present in sediment at concentrations several orders of magnitude higher than its concentration in water (Bowen 1979; Lum and Gamman 1985; Rossman and Barres 1988). Beryllium is so promptly adsorbed from neutral water by mineral and glass surfaces that it can exist in solution only as complexes. Since beryllium in minerals is unlikely to come into contact with high acid or high basic waters, soluble forms of beryllium are highly unlikely in nature. In an extensive study of water samples from the Western United States, beryllium was detected in only three highly acid mine waters. In addition, the chemistry of beryllium shows that at a neutral pH, soluble beryllium salts dissolved in water will be hydrolyzed to insoluble beryllium hydroxide, leaving only trace quantities of dissolved beryllium. Soluble beryllium salts are known to only be created and consumed in the extraction and manufacture of beryllium metals in five locations worldwide, none of which are in the EU. Soluble beryllium salts have no commercial benefit in commerce. Therefore, most of the beryllium in nature is expected to be present either in the sorbed state, in suspended matter, or in the sediment, rather than in the dissolved form, in most natural waters.

Beryllium in Air

Beryllium is naturally emitted to the atmosphere by windblown dusts and volcanic particles. Mineral or soil particles that are sufficiently small may be picked up and carried aloft by surface and prevailing winds. While prevailing winds may carry extremely light particles high into the atmosphere, most particles are too large and too heavy to be carried into the upper atmosphere. A more common fate for these particles is deposition by surface winds onto adjacent land or water surfaces. Beryllium silicate particles from ores are typically far too large and heavy to be taken into the upper atmosphere. Thus, airborne beryllium silicate particles will most likely settle onto adjacent land and water surfaces. (Mason & Dragun 1996)

Human-related sources of beryllium, such as the combustion of coal and fuel oil release, contribute to airborne levels of beryllium. Particles produced from such processes are generally much too large and too heavy to move into the upper atmosphere. (Toxicological Profile for Beryllium – 1991)

The U.S. Agency for Toxic Substances and Disease Registry (ATSDR) has estimated that within the United States, about 45% of airborne beryllium is due to human related releases of beryllium. Natural sources, such as windblown dust and volcanic activity, account for 55% of beryllium released to the atmosphere. Electric utilities comprise about 80% of the emissions, while industry and metal mining accounts for about 20% of the emissions.

Combustion of a beryllium-containing material such as coal or fuel oil releases particulate likely containing beryllium as BeO. Beryllium in coal has been identified as predominantly having an affinity to the organic phase of coal rather than the inorganic phase (mineral phase).

Average Beryllium Content in Coal	1.90 ppm
Average Beryllium Content of Coal Fly Ash	5-16 PPM (USEPA 1978)

Two extremely rare, unstable isotopes of beryllium, 7Be and 10Be, are formed in the upper stratosphere by cosmic ray interactions. The lifetime of 7Be is too short for significant deposition from the stratosphere. The lifetime of 10Be is much longer, but the relative amount of deposition of 10Be from the stratosphere onto terrestrial surfaces is minuscule. Beryllium-containing ore bodies, and consequently products manufactured from these ore-bodies, contain only the stable isotope, 9Be.

No evidence has been established to substantiate that biomethylation or any other environmental process results in the volatilization of beryllium into the atmosphere from soil or water (Bowen 1979).

The average ambient concentration of beryllium in air in the United States is 0.03 ng/m3, while the median concentration in cities is 0.2 ng/m3. Atmospheric beryllium concentrations at rural sites in the U.S. range from 0.03 to 0.06 ng/m3. Lower levels may be found in less industrialized countries. Concentrations of 0.04–0.07 ng/m3 have also been reported at suburban sites and 0.1–0.2 ng/m3 at urban industrial sites. A survey of beryllium concentrations in Japanese cities reported an average concentration of 0.042 ng/m3 and a maximum concentration of 0.222 ng/m3. Urban areas in Germany had beryllium concentrations in air ranging from 0.06 to 0.33 ng/m3.

The U.S. EPA National Emission Standard for beryllium is 0.01 micrograms beryllium per cubic meter of air based on a 30-day average.

Natural beryllium in common materials

Since beryllium occurs naturally in all soil and numerous minerals, it is commonplace to detect natural beryllium in numerous materials/products. Natural forms of beryllium-containing minerals or clays are not intentionally added to such common materials because of the presence of very low levels of minerally-bound beryllium. Natural beryllium does not impart any useful properties to such materials/products nor are there any known health risks associated with exposure to minerally-bound beryllium. High mineral/clay-based content materials/products often contain low parts per million (PPM) concentrations of natural beryllium ranging from 0.5-2 PPM. Examples of high mineral/clay content materials/products that have been found to contain low PPM levels of natural beryllium include:

Portland cement
Ceiling tiles
Bricks
Roofing shingle
Glass wool

Coal
structural and decorative rock
Fertilizers
Sewage sludge

Copper ore
Detergents
Kitty litter
Oil dry
Emery cloth
Grinding wheels

Most common materials/products contain only trace amounts of natural mineral bound beryllium at parts per billion (PPB) levels. Examples of trace mineral/clay-bound beryllium in materials/products that typically contain levels of natural beryllium ranging from <100-500 PPB include:

Metals
Fuel oil
Home barbeque charcoal
Candy wrapper

Cosmetics
Automotive disc brakes
Beach sand
Aluminum foil

Beryllium in plants and foodstuffs

Since beryllium occurs naturally in all soils and sediments, it is commonly found in numerous plants and foodstuffs. The ATSDR reported a median concentration of beryllium in the 38 foods at 22.5 µg/kg (PPB) fresh weight (excluding kidney beans) with a range of concentrations from <0.1–2,200 PPB. The highest concentrations were reported for kidney beans (2200 PPB), crisp bread (112 PPB), garden peas (109 PPB), parsley (77 PPB), and pears (65 PPB). The average concentration of beryllium in fruit and fruit juices is 13.0 µg/L (PPB) with concentrations ranging not detected to 74.9 µg/L. The Mean level of beryllium in clams ranged from <2-15 PPB with an upper value of 20 PPB. With the upper range at Mean levels in fish ranged from 1.5-11PPB with an upper value of 19PPB. No evidence for significant biomagnification of beryllium within food chains has been found (Fishbein 1981). The following are examples from ATSDR 1991/2002.

Solids (µg/Kg/PPB)

Cabbage	0.24	refined sugar	2	carrots	25
Mushrooms	1.58	crisp bread	112	filed corn	25
crabs	15	lettuce	330	peas	109
oyster flesh	2.0	eggplant	370	potatoes	170
rice	80	green pepper	400		
brown sugar	30	kidney beans	2200		

Liquids (µg/L/PPB)

mineral water	0.94 (high) (Kilinc 2011)	Orange juice	2.8 (ATSDR 2002)
wine	0.16- 0.25 (Bayern 2010)	All juices	(detected in 38%) (Bayern 2010)
Whiskey	0.0003 (Woods 2011)		
Apple juice	22.5 (ATSDR 2002) (detected in 58%)	Tomato sauce	42.4 (ATSDR 2002)
		Milk	0.2 µg/kg (ATSDR 2002)

Natural Beryllium in everyday Life

Since beryllium occurs naturally in all soil and numerous minerals, it is commonplace to detect natural beryllium on surfaces in public and private places, including workplaces that do not process materials where beryllium was intentionally added for its unique properties and characteristics. As an example of beryllium in public and private places, Materion Brush Inc. undertook a sampling event in 2002 in Atlanta, Georgia USA. Below are the results from that survey. With regard to the surface sample results, it is important to note that there are no health-based standards for naturally occurring beryllium-containing particulate present on surfaces.

Surface Wipe samples (µg/100 cm^2)	
Country Fried Chicken restaurant	0.036
City Hall newspaper box	0.082
Newspaper stand (downtown)	0.015
Eye exam office	0.012
Big Lot store shelf	0.0085

Soil and other Atlanta area samples (µg/kg/PPB)	
Residential (home) vacuum cleaners	260 & 350
15 soil samples range	<100(2) - 1200
15 soil samples average	563

Beryllium in Non-beryllium manufacturing environments

Beryllium occurs naturally in all soil and numerous minerals and as a result it can be found in materials and products commonly used or found in general manufacturing. Similar to what occurs in public settings, a significant source of beryllium commonly found in general manufacturing and even in office work environments is the result of normal drag-in of soil on shoes. In addition to the drag-in of soil, in general manufacturing settings where materials or products not containing intentionally added beryllium are processed or used, it is common to detect beryllium on surfaces. The largest known study sampling for the presence of beryllium at non-beryllium manufacturing worksites was undertaken by Dr. Field et al. in 2014. Below is a summary from that survey. With regard to the surface sample results, it is important to note that there are no health-based standards for beryllium-containing particulate present on surfaces, no matter whether the source is natural beryllium or intentionally added beryllium. Beryllium surface level guidance does exist for beryllium processing sites for purpose of monitoring levels of cleanliness to support housekeeping efforts. These guidance levels are not derived by an association with a health risk.

Non-beryllium manufacturing facility examples

Surface wipe sampling of visible surface dust (years to decades of accumulation) at 27 businesses not specifically working with beryllium (Field 2014)

- Auto repair shop, coal power plant, flower shop, restaurant, fertilizer co-op, hog confinement, machine shop, electronics shop, dental lab, schools and bars etc.
- 137 samples of surfaces with visible dust (bookshelves, cabinet tops, ductwork, etc.)
- 3 sites (11%) reported prior beryllium use (2 dental labs, 1 machine shop)

78% of samples were above the LOQ (0.035 µg).

12% exceeded 0.2 µg/100 cm2 (6/10 sites w/no beryllium use)
4% exceeded 3 µg/100 cm2 (all prior Be use sites except for the fertilizer co-op)

Findings of interest
Sites without detectable Be:

- electronic shops
- computer recycling shop
- bars/pubs

Sites with detectable Be included:

- flower shop
- hog confinement
- restaurant
- school
- food processing co-op
- fertilizer co-op
- feed/fertilizer shop
- machine shop
- auto repair shop
- power plant
- dental lab
- ceramics shop

Work Activities found to exceed US/EU beryllium OELs of 0.2/0.6 µg/m3 due to exposures to airborne beryllium from working with materials containing trace beryllium that is not intentionally added.

Painting	Road sweeper	Abrasive blasting	Carpentry	Fabricating
Cutting concrete	Road building	Building demolition	Electrical work	Welding
Dumping soils	Jack hammering	Boiler cleaning	Excavating	Sandblasting
Torch cutting	Welding	General labor work	Needle gunning	Shot blasting

Information Source is U.S. OSHA IMIS database

Additionally, a Socio Economic Analysis conducted by RPA UK found that there is a natural presence of beryllium in bauxite, which may cause an exposure in aluminium foundries, as well as a natural presence in fluorite, which may cause an exposure in the glass industry.

Human health risks from exposure to natural beryllium

Health implications for workers exposed to trace beryllium **(not intentionally added)**

- No confirmed known case of CBD linked only to exposures to natural beryllium-containing materials or the use of processed materials where beryllium was not

intentionally added for its unique properties, i.e., abrasive blast media, coal slag in road construction, etc.

- Naturally occurring minerals that contain beryllium involve a form of beryllium that is a beryllium aluminum silicate.

Two published studies have evaluated potential worker health effects from exposures to trace beryllium **(not intentionally added).** Both studies evaluated worker exposures while processing known beryllium-containing minerals (0.4-4% beryllium content).

The only epidemiology study of a worker cohort only exposed to naturally occurring beryllium was by Deubner, et al. 2001. Deubner examined for the beryllium sensitization, chronic beryllium disease and workplace exposures of workers only engaged in the mining of a beryllium ore containing 0.4% beryllium. Deubner concluded:

> "There was no sensitization or CBD among those who worked only at the mine where the only exposure to beryllium is bertrandite ore."

A case control study of gemstone cutters cutting, grinding and polishing beryl stones (aquamarines, emeralds – 4% beryllium) in Germany was pursued by Wegner et al (2000) because of beryllium air sample results having been previously measured ranging from <0.4 – 20 ug/M3 during processing operations. The study performed beryllium sensitization testing on 54 gemstone cutters and 30 controls without contact to beryllium. One of 54 gemstone cutters had a positive test. This subject had a normal X-ray and lung function. For the entire cohort, medical examinations found no clinical abnormalities suggestive of interstitial lung disease in any subject. One subject with a prior diagnosis of sarcoidosis (which can mimic CBD) was found to have a negative beryllium sensitization test and CBD was ruled out. For comparison purpose, it is notable that confirmed beryllium sensitization has been found to occur in the general, non-occupationally exposed population at a rate of about 1%. (Donovan, Kolanz et al. 2002)

Naturally occurring beryllium exposures in non-occupationally exposed persons

Beryllium in the environment will probably be present as beryllium oxide or beryllium hydroxide. Upon reaching water and soil, beryllium will likely be retained in an insoluble form in sediment and will be generally immobile. Although chemical reactions may transform one beryllium compound into another, beryllium cannot be degraded by environmental reactions.

Bioconcentration of beryllium in fish to high levels is not likely due to the low uptake of beryllium from water by aquatic animals. A measured bioconcentration factor (BCF) of 19 is reported for beryllium (EPA 1980). Chemicals with BCFs of < 1000 will not bioaccumulate significantly in aquatic organisms (EPA 1980).

According to the WHO, Beryllium in Drinking Water Background document development of WHO Guidelines for Drinking Water Quality 2009, the general population may be exposed to trace amounts of beryllium by inhalation of air, consumption of drinking-water and food, and inadvertent ingestion of dust. The estimated total daily beryllium intake in the USA was 423 ng, with the largest contributions from food (120 ng/day, based on daily consumption of 1200 g of food containing a beryllium concentration of 0.1 ng/g fresh weight) and drinking-water (300 ng/day, based on daily

intake of 1500 g of water containing beryllium at 0.2 ng/g), with smaller contributions from air (1.6 ng/day, based on daily inhalation of 20 m3 of air containing a beryllium concentration of 0.08 ng/m3) and dust (1.2 ng/day, based on daily intake of 0.02 g/day of dust containing beryllium at 60 ng/g). The concentration used for beryllium in food was the midpoint of a range of values reported for a variety of foods in an Australian survey. The concentration used for beryllium in drinking-water was based on a survey of 1577 drinking-water samples throughout the USA, where beryllium was detected in 5.4% of samples with mean and maximum concentrations of 190 and 1220 ng/l, respectively. The concentration used for beryllium in air was taken as a likely average concentration in a residential area based on air sampling results reported above. The concentration used for beryllium in household dust was estimated by assuming an indoor air concentration of 0.1 ng/m3 and an air to dust ratio of 600. Although intakes from air and dust are minor under background conditions, these can be important pathways of exposure in the vicinity of a point source. Beryllium intake through air and dust can be increased 2–3 orders of magnitude in the vicinity of a point source, such as a coal-fired power plant. Tobacco smoke is another potential source of exposure to beryllium in the general population. Beryllium levels of 0.47, 0.68 and 0.74 µg/cigarette were found in three brands of cigarettes. Between 1.6% and 10% of the beryllium content, or 0.008–0.074 µg/cigarette, was reported to pass into the smoke during smoking. Assuming the smoke is entirely inhaled, an average smoker (20 cigarettes per day) might take in approximately 1.5 µg of beryllium per day (3 times the combined total of the other routes). The U.S. EPA has determined the level of beryllium typically found in human lung tissue at 0.1-20 µg/kg (dry weight) (EPA 1987) with other organs.

Primary References

1. Agency for Toxic Substances and Disease Registry. Toxicological Profile for Beryllium. ATSDR. Atlanta (2002).
2. World Health Organization, Background Document for Development of WHO Guidelines for Drinking water quality (2009).