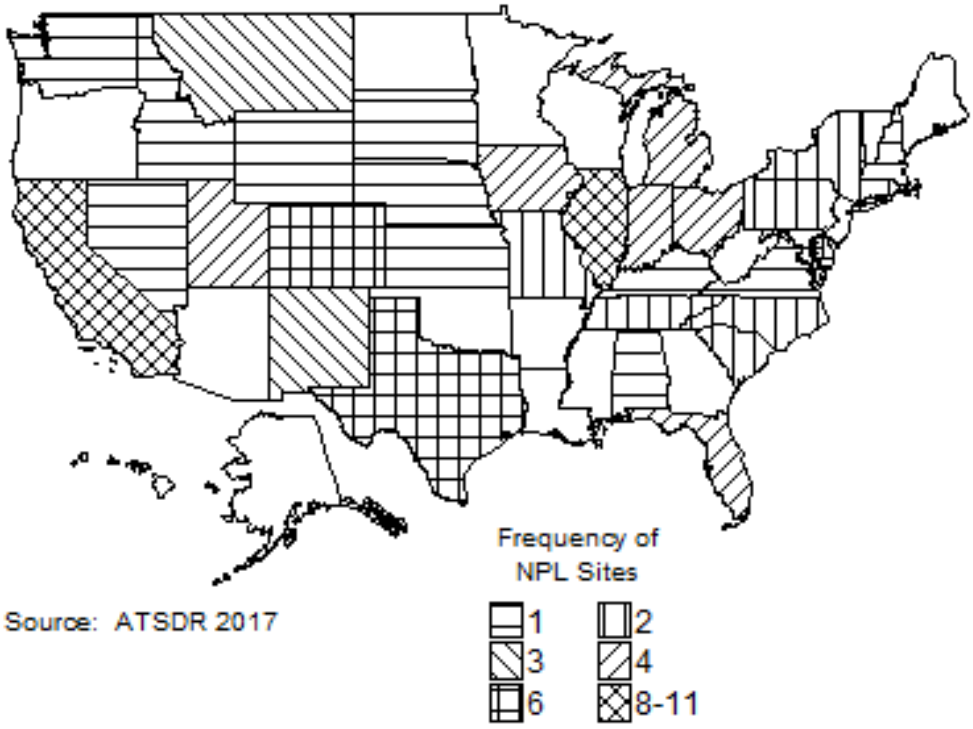
CHAPTER 5. POTENTIAL FOR HUMAN EXPOSURE

5.1 OVERVIEW

Molybdenum has been identified in at least 86 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 molybdenum has been evaluated is not known. The number of sites in each state is shown in Figure 5-1. Of these sites, all are located within the United States.

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



- The general population is primarily exposed to molybdenum through dietary intake.
- Inhalation exposure and ingestion of molybdenum from drinking water is typically low for the general population; however, water levels near mining operations may be higher and exposure may be greater for populations near these activities.
- Molybdenum compounds (e.g., molybdenum trioxide and polymolybdates) transform to the $[MoO_4]^{2-}$ ion under neutral or alkaline conditions; however, protonated forms, such as $[HMoO_4]^-$ and H_2MoO_4, are found at pH <5.

Molybdenum is a naturally occurring trace element found extensively in nature. Biologically, molybdenum plays an essential role as a micronutrient in plants and animals, including humans. It is also used widely in industry for metallurgical applications (EPA 1979). A radioactive isotope of molybdenum (^{99}Mo) is used as a source for producing metastable technetium-99 (^{99m}Tc), which is an important radiopharmaceutical that is used in the vast majority of high resolution medical imaging tests (Parma 2009). Important, naturally occurring molybdenum compounds are the minerals molybdenite, powellite, wulfenite, ferrimolybdite, and ilsemannite. When in the form of molybdate, a tetrahedral polyatomic anion, or other isopolyanions, it can be processed into salts used in industrial applications. The molybdate ion is the most common form of molybdenum found in the aqueous environment (EPA 1979).

If released to the atmosphere, molybdenum will be returned to earth by wet and dry deposition. In water, pH levels and oxidation/reduction conditions of the sediment govern the speciation of molybdenum and adsorption potential in natural aquifers. In the pH range of 3–5, molybdenum tends to exist as hydrogen molybdate and is adsorbed to sediment composed of clay and other oxic minerals (Fitzgerald et al. 2008). The adsorption and mobility of molybdenum in soils is also inversely correlated with pH. Adsorption of molybdenum to 36 surface and subsurface soils was maximized under acidic conditions (pH 2–5) and decreased rapidly at pH 5–8 (Goldberg et al. 2002). The availability of molybdenum to plants and vegetation is also affected by pH and soil properties. Since adsorption to soil decreases with increasing pH, it becomes more bioavailable for uptake to vegetation under nonacidic conditions.

Molybdenum is infrequently detected in ambient air, but is a natural constituent of water and soils. The earth's crust contains an average of 0.0001% (1 ppm) of molybdenum, and surface waters usually have molybdenum concentrations of <5 µg/L (EPA 1979). A decade-long study conducted by the U.S. Geological Survey (USGS) of >5,000 monitoring and drinking water wells from over 40 major aquifers in the United States reported a median molybdenum concentration of 1 µg/L (USGS 2011).

Anthropogenic activities such as mining operations may result in localized areas where molybdenum levels greatly exceed background levels.

The primary route of exposure for the general population to molybdenum is through the ingestion of food. NAS has estimated that the average dietary intakes (AVDIs) of molybdenum by adult men and women are 109 and 76 µg/day, respectively (NAS 2001). Other routes of exposure, such as inhalation of ambient air, ingestion of drinking water, and dermal exposure, are negligible for the general population; however, they may be important routes of exposure in certain occupational settings such as mining activities and

metallurgical applications where molybdenum is used. For example, molybdenum levels in air samples of two plants that produce molybdenum salts were 0.5–200 and 0.2–30 mg/m^3, depending upon the location of the sample and operation being performed (EPA 1979). Respirable dust samples contained molybdenum at levels of 0.471, 1.318, 0.142, and 0.318 mg/m^3 during mining, crushing, milling, and open pit operations, respectively, at a Colorado mine (EPA 1979).

The extensive nationwide use of radioactive ^{99}Mo in generators that produce ^{99m}Tc for nuclear medicine imaging scans can expose medical staff and the public in medical facilities to low levels of ionizing radiation. The extent of those exposures is limited by U.S. Nuclear Regulatory Commission (USNRC) and agreement state regulations (USNRC 2016a, 2016b).

5.2 PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2.1 Production

Molybdenum is a naturally occurring trace element that can be found extensively in nature. Biologically, it plays an important role as a micronutrient in plants and animals, including humans. It is also used widely in industry for metallurgical applications (USGS 2015a).

Molybdenum does not occur naturally in the pure metallic form, but is in minerals, principally as oxide or sulfide compounds (Barceloux 1999; EPA 1979). Important naturally occurring molybdenum compounds are the minerals molybdenite (MoS_2, the predominant source), powellite, wulfenite, ferrimolybdite, and ilsemannite. Molybdenum may also form molybdate, a tetrahedral poly atomic anion, or other isopolyanions, which can form salts used in industrial applications. The earth's crust contains an average of 0.0004% (4 ppm) of molybdenum (Sebenik et al. 2012). Deposits that are economically feasible for mining contain ≥200 ppm of molybdenum, with lower concentrations obtained as a byproduct of copper mining (EPA 1979).

Molybdenite (MoS_2) is the principal mineral from which molybdenum is obtained. Mining and milling of crude ore produce molybdenite concentrate containing ≥90% of MoS_2, almost all of which is converted to technical-grade molybdenum trioxide. Molybdenum trioxide is the base material for the production of a variety of chemical compounds, ferromolybdenum, and purified molybdenum (EPA 1979).

Roasting molybdenite concentrate in a multiple hearth furnace at temperatures up to 600°C produces technical-grade molybdenum trioxide. This can be further purified by sublimation or selective recrystallization at about 1,000–1,100°C (Sebenik et al. 2012).

Worldwide mine production of molybdenum was estimated to be 258,000 metric tons in 2013, with approximately 92% produced, in descending order, by China, the United States, Chile, Peru, Mexico, and Canada. The United States accounted for 24% of world production with 60,700 metric tons in 2013, down slightly from 61,500 metric tons in 2012. Primary molybdenum operations accounted for 53% of total U.S. molybdenum production, while byproduct production made up 47% of the total in 2013. All U.S. molybdenum concentrates and products are from the mining of ore (USGS 2015a). U.S. production of molybdenum increased roughly 8% in 2014 to 65,500 metric tons (USGS 2015b). U.S. production of molybdenum for 2018 was 41,900 metric tons (USGS 2019). The USGS Mineral Industry Survey for molybdenum reported that domestic production for the first 3 months of 2019 was 3,620 metric tons (January), 3,420 metric tons (February) and 3,650 metric tons (March) (USGS 2019).

Table 5-1 contains a list the number of facilities per state that produced, processed, or used molybdenum trioxide in 2017, as well as information on the amount of molybdenum trioxide on site and related activities and uses (TRI17 2018).

Table 5-1. Facilities that Produce, Process, or Use Molybdenum Trioxide

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
AL	5	100	99,999	7, 10, 12
AR	2	100,000	999,999	7
AZ	3	100,000	9,999,999	1, 4, 7, 9
CA	16	1,000	9,999,999	1, 2, 3, 7, 9, 10, 12, 13
CO	1	100,000	999,999	1, 6, 12, 13
DE	1	0	99	12
GA	1	0	0	0
IA	3	1,000,000	9,999,999	1, 3, 4, 6, 9
ID	1	10,000	99,999	12
IL	8	10,000	999,999	1, 5, 6, 7, 10
IN	7	1,000	999,999	1, 5, 6, 7, 8, 9, 10
KS	4	0	999,999	2, 3, 8, 10
KY	5	10,000	999,999	1, 2, 3, 4, 6, 7, 10
LA	27	0	49,999,999	1, 2, 3, 5, 6, 7, 8, 9, 10, 11, 12, 13

Table 5-1. Facilities that Produce, Process, or Use Molybdenum Trioxide

State[a]	Number of facilities	Minimum amount on site in pounds[b]	Maximum amount on site in pounds[b]	Activities and uses[c]
MD	1	100,000	999,999	7
ME	1	10,000	99,999	1, 5, 6
MI	4	0	99,999	1, 5, 6, 7, 10
MN	3	10,000	9,999,999	1, 7, 9, 10, 11, 13
MS	2	10,000	999,999	1, 5, 7, 10
MT	3	10,000	999,999	1, 2, 3, 5, 10, 12, 13
ND	2	10,000	99,999	10
NE	1	10,000	99,999	10
NJ	2	100,000	999,999	10
NM	2	10,000	999,999	10
NV	1	10,000	99,999	12
OH	8	1,000	999,999	1, 6, 7, 8, 9, 11, 13
OK	4	10,000	999,999	1, 4, 5, 7, 10, 13
OR	1	10,000	99,999	7
PA	17	100	9,999,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12
TX	40	0	99,999,999	1, 2, 3, 4, 6, 7, 8, 9, 10, 11, 12
UT	3	100	999,999	10, 11
WA	3	1,000	999,999	7, 10, 11, 12
WI	1	10,000	99,999	10, 11
WV	2	10,000	9,999,999	2, 3, 7, 10
WY	3	10,000	999,999	10

[a]Post office state abbreviations used.
[b]Amounts on site reported by facilities in each state.
[c]Activities/Uses:

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

Source: TRI17 2018 (Data are from 2017)

Molybdenum-99 (^{99}Mo) is a radioactive form of molybdenum and the only molybdenum radioisotope of commercial importance. It is produced in nuclear reactors, and then processed, packaged, and shipped to medical facilities throughout the world, where the ^{99}Tc progeny into which it transforms is eluted and injected into patients for imaging purposes (e.g., cardiac stress tests).

^{99}Mo was produced in one of eight nuclear reactors (mainly at the Chalk River complex in Canada) using highly enriched uranium, and then commercialized at five processing facilities and six generator manufacturing facilities. The availability of those reactors was reduced by the closure of the Chalk River facility, and this impacted the supply stream. The United States has established a high national priority on assuring an adequate supply of ^{99}Mo and urged manufacturers to switch from using highly enriched uranium (HEU) to low enriched uranium (LEU) to reduce the use of HEU for civilian applications (Ballinger 2010; The White House 2012; USNRC 2015; Van Noorden 2013). At a NAS symposium in 2017, several companies discussed their plans to produce ^{99}Mo in the United States (NAS 2018).

Currently, ^{99}Mo can be produced by placing HEU or LEU targets in an operating nuclear reactor and allowing the neutron flux to produce ^{99}Mo and its radioactive precursors. The quantity of ^{99}Mo peaks after approximately 6 days, at which time, the target is removed, processed, and prepared for shipment. New facilities for producing ^{99}Mo from LEU in the United States are being planned (Welsh et al. 2015).

5.2.2 Import/Export

Molybdenum-containing exports rose from 49,900 metric tons in 2010 to 55,300 metric tons in 2014, while imports for consumption rose from 19,700 metric tons in 2010 to 23,600 metric tons in 2014 (USGS 2015b). Imports of molybdenum (excluding ore) were 22,190 metric tons in 2018 and exports totaled 44,700 metric tons (USGS 2019). These data, along with U.S. production volumes, are summarized in Table 5-2.

Table 5-2. Molybdenum U.S. Production, Import, and Export Data from 2010 to 2014 and 2018 in Metric Tons

	2010[a]	2011[a]	2012[a]	2013[a]	2014[a]	2018[b]
Total U.S. production	59,400	63,700	61,500	60,700	65,500	41,900
U.S. imports for consumption	19,700	21,100	19,800	20,200	23,600	22,219[c]
U.S. exports for consumption	49,900	56,700	48,900	53,100	55,300	44,700[d]

[a]USGS 2015b.
[b]USGS 2019.
[c]Excludes imports of ore and concentrate.
[d]Includes ores and concentrates.

5.2.3 Use

Molybdenum is used primarily in metallurgical applications, including as an alloying agent in cast iron, steel, and superalloys to enhance properties such as hardenability, strength, toughness, and wear- and corrosion-resistance. Molybdenum is commonly used in combination with other alloy metals like chromium, cobalt, manganese, nickel, niobium, and tungsten. The leading form of molybdenum used by industry, particularly in stainless steel production, is molybdenum trioxide (USGS 2015a).

Molybdenum is used significantly as a refractory metal and molybdenum compounds in a variety of non-metallurgical chemical applications, such as catalysts, lubricants, and pigments. For example, MoS_2 is used along with cobalt during the desulfurization process of petroleum (Sebenik et al. 2012). Most molybdenum nitride catalysts are nitrogen deficient due to thermodynamically unfavorable conditions at atmospheric pressure; however, molybdenum nitride was recently produced in a high temperature and pressure environment by solid state ion exchange. Testing found its catalytic activity to be 3 times that of MoS_2 and its selectivity to hydrogenation to be 3 times that of MoS_2 for hydrodesulfurizing dibenzo-thiophene (Wang et al. 2015). As green technology is becoming more popular, molybdenum has become increasingly important in areas like biofuels, catalysts, ethanol, solar panels, and wind power (USGS 2015a).

A radioactive isotope of molybdenum, ^{99}Mo, is used as a source to produce the metastable radioisotope technetium-99m (^{99m}Tc), which is used in the vast majority of medical imaging tests performed today (Doll et al. 2014; Parma 2009; Richards 1989). It was estimated that 85% of all medical radioisotope procedures use ^{99m}Tc and that about 50,000 ^{99m}Tc-based diagnostic procedures are performed in the United States each day, resulting in about 13 million procedures annually (Parma 2009).

Molybdenum concentrate produced by U.S. mines is roasted, exported for conversion, or purified to lubricant-grade molybdenum disulfide. Purified MoS_2 is used directly as a solid or in coatings that are bonded onto the metal surface by burnishing, vapor deposition, or bonding processes that use binders, solvents, and mechanochemical procedures (Stiefel 2011).

Metallurgical applications accounted for about 87% of total molybdenum use in 2013. The principle non-metallurgical use was in catalysts, primarily catalysts used in petroleum refining. Molybdenum compounds are also used to produce pigments (USGS 2015a).

5.2.4 Disposal

Recycling is the most environmentally acceptable means of disposal for stable molybdenum (USGS 2015b). Because molybdenum is difficult to remove from waste water, it often is adsorbed to biosolids in municipal waste water treatment facilities. Biosolids are beneficial and are often used as fertilizer or compost for agricultural applications. In the United States, the land application ceiling limit for molybdenum in biosolids is 75 mg/kg (EPA 2018b).

A ^{99m}Tc generator containing a depleted uranium shield or sufficient residual ^{99}Mo radioactivity to be considered radioactive can be disposed of by shipping to an authorized licensee following USNRC agreement state requirements along with those of the Department of Transportation (USNRC 2015). If the ^{99}Mo is allowed to decay sufficiently (typically ≥10 half-lives) and the internal shield is lead or tungsten, then disposal should follow state and local requirements.

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).

Molybdenum mining, milling, and smelting, along with its association with uranium mining and milling, copper mining and milling, shale oil production, oil refining, and coal-fired power plants, have resulted in major releases to the environment (EPA 1979).

5.3.1 Air

Estimated releases of 83,484 pounds (~37.87 metric tons) of molybdenum trioxide to the atmosphere from 188 domestic manufacturing and processing facilities in 2017, accounted for about 4.23% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2018). These releases are summarized in Table 5-3.

Table 5-3. Releases to the Environment from Facilities that Produce, Process, or Use Molybdenum Trioxide[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
AL	5	59	0	0	8,295	0	4,539	3,815	8,354
AR	2	105	0	0	0	4,398	105	4,398	4,503
AZ	3	7,400	0	0	14,011	5	7,400	14,016	21,416
CA	16	638	43	0	11,305	70,649	10,152	72,484	82,635
CO	1	26	0	0	0	0	26	0	26
DE	1	14	0	0	2	0	14	2	15
GA	1	0	0	0	0	0	0	0	0
IA	3	8,650	6,100	0	5,705	0	15,500	4,955	20,455
ID	1	3	0	0	22,265	0	22,268	0	22,268
IL	8	18,361	2,685	0	16,464	2,449	21,046	18,913	39,959
IN	7	394	12,002	0	420,655	3,091	73,394	362,748	436,142
KS	4	250	0	0	5	0	255	0	255
KY	5	297	0	0	1,071	21	307	1,082	1,390
LA	27	6,761	1,733	81,533	279,468	9,012	258,237	120,270	378,507
MD	1	500	6,500	0	250	0	7,250	0	7,250
ME	1	147	0	0	0	0	147	0	147
MI	4	5	44	0	0	0	49	0	49
MN	3	124	5	0	227	0	129	227	356
MS	2	85	740	0	3,100	0	825	3,100	3,925
MT	3	129	0	0	24	0	129	24	153
ND	2	3	0	0	46	0	3	46	49
NE	1	0	0	0	0	0	0	0	0
NJ	2	0	0	0	13,620	0	0	13,620	13,620
NM	2	3	0	0	0	0	3	0	3
NV	1	1	0	0	42,143	0	42,144	0	42,144
OH	8	281	2,029	50,320	547	83	50,606	2,654	53,259
OK	4	3,501	20	0	0	46,900	3,521	46,900	50,421

Table 5-3. Releases to the Environment from Facilities that Produce, Process, or Use Molybdenum Trioxide[a]

		Reported amounts released in pounds per year[b]							
							Total release		
State[c]	RF[d]	Air[e]	Water[f]	UI[g]	Land[h]	Other[i]	On-site[j]	Off-site[k]	On- and off-site
OR	1	17	0	0	1,266	0	1,153	130	1,283
PA	17	25,837	743	0	25,890	340	46,536	6,274	52,810
TX	40	9,616	6,224	54,360	659,999	0	593,414	136,784	730,199
UT	3	12	0	0	60	0	12	60	72
WA	3	260	0	0	7	0	260	7	267
WI	1	0	0	0	0	0	0	0	0
WV	2	0	0	0	0	0	0	0	0
WY	3	5	0	0	0	0	5	0	5
Total	188	83,484	38,868	186,213	1,526,424	136,948	1,159,428	812,509	1,971,937

[a]The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. Data are rounded to nearest whole number.
[b]Data in TRI are maximum amounts released by each facility.
[c]Post office state abbreviations are used.
[d]Number of reporting facilities.
[e]The sum of fugitive and point source releases are included in releases to air by a given facility.
[f]Surface water discharges, waste water treatment-(metals only), and publicly owned treatment works (POTWs) (metal and metal compounds).
[g]Class I wells, Class II-V wells, and underground injection.
[h]Resource Conservation and Recovery Act (RCRA) subtitle C landfills; other onsite landfills, land treatment, surface impoundments, other land disposal, other landfills.
[i]Storage only, solidification/stabilization (metals only), other off-site management, transfers to waste broker for disposal, unknown
[j]The sum of all releases of the chemical to air, land, water, and underground injection wells.
[k]Total amount of chemical transferred off-site, including to POTWs.

RF = reporting facilities; UI = underground injection

Source: TRI17 2018 (Data are from 2017)

The primary source of molybdenum emissions to the atmosphere is coal combustion. In 1970, it was estimated that 550 metric tons of molybdenum were released via coal combustion in the United States, in comparison to 900 metric tons estimated from all air pollution sources (EPA 1979). A total of 909 metric tons of molybdenum can be emitted from a single 1,000 megawatt power plant per year (EPA 1979). Historical concentrations of molybdenum in fly ash from coal combustion were reported to range from 7 to 160 mg/kg (Barceloux 1999). Advances in sorbent and air pollution control technology such as fabric filters and electrostatic precipitators in power plants have resulted in a reduction of atmospheric emissions of molybdenum and other metals as compared to emissions from decades ago (Cho and Wu 2004; EPA 2009a). A report from the EPA, which compiled data on 73 coal combustion residues (CCR),

typically found molybdenum levels of 8–30 µg/g (mg/kg) in fly ash and scrubber sludges and about 1–10 µg/g (mg/kg) in gypsum (EPA 2009a). The study reported that no correlation was observed in molybdenum content and coal type or air pollution control system employed.

5.3.2 Water

Estimated releases of 38,868 pounds (~17.63 metric tons) of molybdenum trioxide to surface water from 188 domestic manufacturing and processing facilities in 2017, accounted for about 1.97% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2018). This estimate includes releases to waste water treatment and publicly owned treatment works (POTWs) (TRI17 2018). These releases are summarized in Table 5-3.

Per year, it has been estimated that natural processes result in the release of $3.6x10^{10}$ g of molybdenum into surface waters (EPA 1979).

Aqueous effluents from industries with a high presence of molybdenum, including molybdenum mining, milling, and smelting; uranium mining and milling; copper mining and milling; shale oil production; oil refining; and coal-fired power plants, contain molybdenum at concentrations ranging from 100 to 800,000 µg/L (EPA 1979). Molybdenum levels in leachate samples obtained from a landfill located in Caledonia, Wisconsin ranged from 1.28 to 16 µg/L (WDNR 2013).

Effluent concentrations of molybdenum from three molybdenum mining and milling operations (two in Colorado, one in New Mexico) ranged on the order of 1,000–10,000 µg/L. In 1972, a mine in Colorado released approximately 100,000 kg of molybdenum into a receiving stream. Releases of molybdenum from coal power plants to surface waters in the United States average about 1,800 metric tons/year. A uranium mill in Colorado reported leaking of the tailings ponds containing 860,000 µg/L molybdenum in 1965. Some uranium operations in New Mexico reported as much as 1,000 µg/L molybdenum in aqueous effluents. Copper milling operations have reported molybdenum effluent concentrations as high as 30,000 µg/L (EPA 1979).

Frasacoli and Hudson-Edwards (2018) compiled monitoring data on molybdenum levels in mining-affected areas in different parts of the world, which included groundwaters, nearby rivers, and tailing pore water. The largest levels of molybdenum were observed in mine waste from a coal mine located in Poland (2,332,000 µg/L). Groundwater from an area near 13 nonactive mines in Mexico ranged from

<5 to 150 µg/L. Tailing pore water from an inactive mining operation in Manitoba, Canada had molybdenum levels of <5–1,100 µg/L. Molybdenum concentrations from tailings channel water from an active copper mining facility in Chile ranged from 2,670 to 3,900 µg/L. Mine drainage samples obtained from an operational mine in Peru had molybdenum levels of 0.001–13.9 ppm (1–13,900 µg/L) (Skierszkan et al. 2016).

5.3.3 Soil

Estimated releases of 1,526,424 pounds (~692.37 metric tons) of molybdenum trioxide to soil from 188 domestic manufacturing and processing facilities in 2017, accounted for about 77.41% of the estimated total environmental releases from facilities required to report to the TRI (TRI17 2018). An additional 186,213 pounds (~84.46 metric tons), accounted for about 9.44% of the total environmental emissions, were released via underground injection (TRI17 2018). These releases are summarized in Table 5-3.

Metals, such as molybdenum, may leach into soil via municipal solid waste incineration bottom ash (IMOA 2015).

5.4 ENVIRONMENTAL FATE

5.4.1 Transport and Partitioning

Air. Molybdenum released to the air by industrial processes will be subject to atmospheric deposition (IMOA 2015). Deposition from the atmosphere is only a minor source to terrestrial and aquatic environments (Fitzgerald et al. 2008).

Water. Molybdenum can be leached into the aquatic environment near industrial use areas via direct release or atmospheric wet deposition by rain (IMOA 2015). The pH of water, along with the composition and redox conditions of the sediment, greatly affect the speciation and adsorption behavior of molybdenum in natural waterbodies. Molybdenum accumulation in the sediment phase is favored under conditions of low pH and in sediments with low redox potential and high iron and organic matter content (Fitzgerald et al. 2008). In more favorable reducing geochemical conditions, solid-phase iron and manganese oxyhydroxides tend to undergo dissolution, and sorbed molybdenum may be released back into the water phase.

Sediment and Soil. In a seasonally anoxic basin, the distribution of molybdenum in the pore water of sediments was relatively uniform. In a perennially oxic basin, however, there was a redistribution of molybdenum in the sediment-water interface subsequent to deposition. This was determined to be a consequence of adsorption of molybdenum to iron oxyhydroxides at a rate of 36 cm^3/molecule-second in the first 1–2 cm depth (IMOA 2015).

Geological uplift and atmospheric deposition result in the molybdenum enrichment of surface soils (IMOA 2015). Molybdenum concentrations are found to be the highest in the topsoil layer, due to strong binding to natural organic matter. Goldberg et al. (2002) studied the adsorption potential of molybdenum as a function of pH on 36 surface and subsurface soil samples from 27 soil series belonging to six different soil orders, which provided a wide range of soil physical-chemical characteristics such as organic carbon content, cation exchange capacity, and iron content. In general, maximum adsorption occurred under acidic pH conditions (pH 2–5) in which molybdenum adsorbed to oxyhydroxide mineral surfaces and sorption decreased rapidly from pH 5 to 8 and was minimal in all soils at pH >9. Skierszkan et al. (2016) studied the stable isotopic composition of molybdenum and zinc in mine wastes and noted a large variation in δ^{98}Mo (a measure of how the isotopic composition in the liquid or solid waste differed from a National Institute of Standards and Technology [NIST] standard solution) as a function of adsorption. At lower pH, adsorption of molybdenum is greatest, and the molybdenum isotope profile shifts toward heavier isotopic composition, as the adsorption process preferentially removes lighter isotopes. In contrast, zinc has the opposite behavior as it is more mobile under acidic conditions and adsorption is enhanced under alkaline conditions with lighter zinc isotopes more prominent. These results suggest the possibility of using isotopic composition as a method to understand attenuation mechanisms such as adsorption and molybdate precipitation during the weathering process.

Other Media. As reviewed by Regoli et al. (2012), the bioaccumulation factor (BAF) ranged from 30.1 to 71.6 (average of 49) in fish exposed to molybdenum levels <65 ug/L. At higher molybdenum levels (up to 766 µg/L), the BAF ranged from 0.4 to 9.9 (average 1.4). A laboratory study in rainbow trout found a similar inverse relationship between molybdenum concentration in the water and bioconcentration factor (BCF) (Regoli et al. 2012). A 60-day exposure to 880 µg/L resulted in tissue levels below the limit of detection. Exposure to 11,100 µg/L for 28 days resulted in whole-body molybdenum levels of 0.53 mg/kg fish; the calculated average BCF was 0.05. In another study, fish in a creek near a molybdenum tailings pile had measured BCFs of <100 after a 2-week exposure (CCME 1999). The accumulation data show that the BAF decreases with increasing molybdenum levels. At low

molybdenum concentrations, there is an active accumulation of essential metals in organisms (and often non-essential metals via the same uptake mechanisms) to ensure that metabolic requirements are met. This active uptake process decreases when organisms are exposed to higher metal concentrations. At higher concentrations, organisms with active regulation mechanisms are even limiting their uptake by excretion of excess metals. EPA published a framework for metals risk assessment that discusses the difference in interpreting BCF and BAF values for organic versus inorganic compounds (EPA 2017a). It was generally concluded that the most recent scientific data on bioaccumulation do not currently support the use of BCF and BAF values when applied as generic threshold criteria when assessing the hazardous potential of metals. Moreover, single-value BCF/BAF data are most applicable to site-specific assessments; for more general regional or national assessments, the media chemistry and metal concentrations for a particular species should be considered for BCF/BAF studies.

5.4.2 Transformation and Degradation

As a naturally occurring trace element, molybdenum can be found extensively in nature. The predominant form of molybdenum in natural waters is as the molybdate anion, $[MoO_4]^{2-}$ (Barceloux 1999), while naturally occurring molybdenum salts are the dominant form in dry environments (EPA 1979).

Air. No information regarding the chemical forms of molybdenum in the atmosphere and their transformations could be located. It is generally assumed that metals, especially those from combustion sources, exist in the atmosphere as oxides since metallic species are readily attacked by atmospheric oxidants.

Water. The speciation of molybdenum in aqueous media as a function of pH and molybdenum concentration, has been thoroughly investigated and reported upon in open literature. As discussed in Chapter 4, at pH >6.5, the sole molybdenum species is the molybdate anion, $[MoO_4]^{2-}$ (Cruywagen 2000; Cruywagen et al. 2002). Molybdenum compounds transform rapidly into the $[MoO_4]^{2-}$ ion under environmentally relevant conditions (Greenwood and Earnshaw 1997). In low redox environments, the molybdate anion can be reduced to molybdenum disulfide or molybdenite (Fitzgerald et al. 2008).

Sediment and Soil. Molybdenum is found naturally in soil as the minerals molybdenite, powellite, wulfenite, ferrimolybdite, and ilsemannite (EPA 1979; Fitzgerald et al. 2008).

The predominant form of molybdenum in wet soil is as the molybdate anion, $[MoO_4]^{2-}$ (Barceloux 1999).

Other Media. No data for the degradation of molybdenum in other media were located.

5.5 LEVELS IN THE ENVIRONMENT

Reliable evaluation of the potential for human exposure to molybdenum depends, in part, on the reliability of supporting analytical data from environmental samples and biological specimens. Concentrations of molybdenum 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 molybdenum 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 5-4 shows the typical limits of detection that are achieved by commonly employed analytical methods in environmental media. Smedley and Kinniburgh (2017) compiled a list of ranges for molybdenum in environmental matrices from primary references, including analytical detection limits. The American Public Health Association publishes analytical methods for molybdenum and other metals in aqueous samples and the EPA publishes laboratory analytical methods and procedures to test for analytes in air, water, solids, and hazardous waste. An overview summary of the range of concentrations detected in environmental media is also presented in Table 5-5.

Table 5-4. Lowest Limit of Detection Based on Standards[a]

Media	Detection limit	Reference
Air	0.48 ng/m^3	EPA 1999 (Method IO-3.3)
Drinking water	0.3 µg/L	EPA 1994 (Method 200.8)
Surface water and groundwater	0.3 µg/L; 8 µg/L	APHA 1989 (Method 3120B); EPA 1994 (Method 200.8)
Soil	0.000090–0.0023 mg/kg	Campillo et al 2002
Sediment	0.000090–0.0023 mg/kg	Campillo et al. 2002
Whole blood	~0.1 ng/mL (µg/L)	Keyes and Turnland (2002)

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

Table 5-5. Summary of Environmental Levels of Molybdenum

Media	Low	High	For more information
Outdoor air (µg/m^3)	0.2	8.05	Section 5.5.1
Surface water (µg/L)	<1	157	Section 5.5.2
Groundwater (µg/L)	1	4,700	Section 5.5.2
Drinking water (µg/L)	<1	>40	Section 5.5.2
Food (ppb)	<1	1,800	Section 5.6
Soil (mg/kg)	<0.05	94.7	Section 5.5.3

Detections of molybdenum in air, water, and soil at NPL sites are summarized in Table 5-6.

Table 5-6. Molybdenum Levels in Water, Soil, and Air of National Priorities List (NPL) Sites

Medium	Median[a]	Geometric mean[a]	Geometric standard deviation[a]	Number of quantitative measurements	NPL sites
Water (µg/L)	340	229	14.4	16	10
Soil (mg/kg)	57	56.2	0.00794	7	6
Air (µg/m$^{3)}$	0.0655	0.0515	2.30	4	2

[a]Concentrations found in ATSDR site documents from 1981 to 2017 for 1,854 NPL sites (ATSDR 2017). Maximum concentrations were abstracted for types of environmental media for which exposure is likely. Pathways do not necessarily involve exposure or levels of concern.

5.5.1 Air

Molybdenum concentrations in ambient air have been reported to range from below detection limits to 0.03 mg/m^3 (EPA 1979). Concentrations of molybdenum in ambient air of urban areas, 0.01–0.03 µg/m^3, are higher than those found in rural areas, 0.001–0.0032 µg/m^3 (Barceloux 1999). Data from the EPA Air Quality System Database reported 24-hour concentrations of molybdenum at several locations in the United States for 2018 (EPA 2018c). These data are summarized in Table 5-7.

Table 5-7. 24-Hour Molybdenum Concentrations (µg/m^3) in Air Samples (2018 Data)

State (sample type)	Arithmetic mean	99th percentile	75th percentile	50th Percentile	10th Percentile
California (TSP)	0.0007	0.0015	0.0007	0.0007	0.0007
California (TSP)	0.0008	0.0019	0.0007	0.0007	0.0007
California (TSP)	0.0009	0.0016	0.0015	0.0007	0.0007
California (TSP)	0.0015	0.0053	0.0019	0.0007	0.0007
California (TSP)	0.0010	0.0023	0.0015	0.0007	0.0007
California (TSP)	0.0030	0.0063	0.0042	0.0028	0.0007
California (TSP)	0.0037	0.0068	0.0047	0.0038	0.0007
California (TSP)	0.0008	0.0016	0.0007	0.0007	0.0007
California (TSP)	0.0009	0.0023	0.0007	0.0007	0.0007
California (TSP)	0.0008	0.0019	0.0007	0.0007	0.0007
California (TSP)	0.0008	0.0021	0.0007	0.0007	0.0007
California (TSP)	0.0013	0.0042	0.0015	0.0007	0.0007
California (TSP)	0.0010	0.0026	0.0015	0.0007	0.0007
California (TSP)	0.0010	0.0025	0.0015	0.0007	0.0007
California (TSP)	0.0015	0.0046	0.0019	0.0007	0.0007
California (TSP)	0.0007	0.0014	0.0007	0.0007	0.0007
California (PM_{10})	2.0000	2.0000	2.0000	2.0000	2.0000
California (PM_{10})	2.0000	2.0000	2.0000	2.0000	2.0000
California (PM_{10})	0.0002	0.0020	0.0000	0.0000	0.0000
California ($PM_{2.5}$)	0.0003	0.0030	0.0000	0.0000	0.0000
California ($PM_{2.5}$)	0.0001	0.0030	0.0000	0.0000	0.0000
California ($PM_{2.5}$)	0.0003	0.0030	0.0000	0.0000	0.0000
California ($PM_{2.5}$)	0.0003	0.0030	0.0000	0.0000	0.0000
California ($PM_{2.5}$)	0.0003	0.0020	0.0000	0.0000	0.0000
California ($PM_{2.5}$)	0.0013	0.0043	0.0017	0.0010	0.0004
Michigan (TSP)	0.0011	0.0026	0.0016	0.0010	0.0002
Michigan (TSP)	3.0787	49.5000	1.4000	0.9000	0.5000
Michigan (PM_{10})	0.9935	2.2000	1.5000	0.9000	0.4000
Michigan (PM_{10})	1.0057	2.6000	1.4000	0.8000	0.4000
Michigan (PM_{10})	1.1778	2.4000	1.5000	1.1000	0.4000
Texas ($PM_{2.5}$)	0.0005	0.0040	0.0010	0.0000	0.0000

Table 5-7. 24-Hour Molybdenum Concentrations (µg/m^3) in Air Samples (2018 Data)

State (sample type)	Arithmetic mean	99th percentile	75th percentile	50th Percentile	10th Percentile
Texas ($PM_{2.5}$)	0.0006	0.0030	0.0010	0.0000	0.0000
Texas ($PM_{2.5}$)	0.0006	0.0020	0.0010	0.0000	0.0000
Vermont ($PM_{2.5}$)	0.0726	0.4700	0.1100	0.0400	0.0100
Vermont (PM_{10})	0.0655	0.2700	0.1100	0.0400	0.0000
Vermont (PM_{10})	0.1955	0.3800	0.2700	0.1500	0.0900
Vermont (PM_{10})	0.1787	0.5900	0.3000	0.1000	0.0400

PM_{10} = particulate matter ≤10 µm in diameter; $PM_{2.5}$ = particulate matter ≤2.5 µm in diameter; TSP = total suspended particulate

Source: EPA 2018c

5.5.2 Water

It has been reported that concentrations of molybdenum are generally <1.0 µg/L in surface waters (USGS 2006) and 1.0 µg/L in drinking water (USGS 2011). Groundwaters contain about 1.0 µg/L (USGS 2011). Smedley and Kinniburgh (2017) compiled ranges of molybdenum levels in rain water, stream water, rivers, lakes, estuaries, and oceans. Most surface water levels were <1 µg/L; however, there was wide variability, with levels tending to be higher with increasing salinity of the body of water (for example, molybdenum levels in the Salton Sea, California were reported as high as 37 µg/L).

A USGS study of surface water from 51 of the nation's major river basins was conducted from 1991 to 2002 (USGS 2006). The median concentration of molybdenum in 2,773 surface water samples was <1.0 µg/L, with a maximum concentration of 157 µg/L. There were eight samples (approximately 0.29% of the total) that exceeded the health-based screening level of 40 µg/L for molybdenum.

In a study of surface waters collected from 197 sampling stations in Colorado, molybdenum was found at concentrations <10 µg/L in 87% of the 299 samples. Samples that contained concentrations >5 µg/L were concluded to be the result of proximity to mineralization or mining and milling operations (EPA 1979). However, another study comparing surface waters draining highly mineralized areas to those with baseline molybdenum areas found that molybdenum mineralization did not contribute significantly to

concentrations in surface waters. The waters from streams draining the highly mineralized areas rarely had molybdenum concentrations above 1–2 µg/L (EPA 1979).

Huang et al. (2010) discussed surface water concentrations of metals including molybdenum in the Gyama Valley, an area impacted by four metal mining operations. Molybdenum concentrations ranged from <0.6 (detection limit) to 10.4 µg/L in the Gyamaxung-chu stream/river.

DOI (1967) collected river and lake water samples from 100 sampling stations around the United States from 1962 to 1967. The samples were taken from areas susceptible to contamination, including highly populated areas, industrial areas, recreational use areas, and state and national boundaries. Molybdenum was detected in the water samples at maximum concentrations >100 µg/L at 38 of the sample sites, while 26 sites had mean molybdenum concentrations >50 µg/L.

Molybdenum levels of 9.3–10.4 µg/L for open oxic seawater and 0.67–3.74 µg/L in euxinic waters of the Black Sea were reported (Smedley and Kinniburgh 2017). Kulathilake and Chatt (1980) reported the molybdenum concentration in the Atlantic Ocean as 7.2–7.9 µg/L. Another study reported that the molybdenum concentration in the North Atlantic ranged from 0.5 to 1.0 µg/L (Chan and Riley 1966). In the Pacific Ocean, measured molybdenum concentrations included 8.8 µg/L in the Eastern Pacific (Kiriyama and Kuroda 1984) and 1.5 µg/L in the Western Pacific (Nakata et al. 1983). Kawabuchi and Kuroda (1969) reported a mean molybdenum concentration of 7.7 µg/L in Tokyo Bay. Molybdenum concentrations measured in the English Channel ranged from 12 to 16 µg/L (Chan and Riley 1966), while the Irish Sea was reported to have a mean molybdenum concentration of 8.4 µg/L (Riley and Taylor 1968).

A comprehensive groundwater monitoring study conducted from 1992 to 2003 by the USGS of 5,183 monitoring and drinking-water wells representative of over 40 principal aquifers in humid and dry regions and in various land-use settings reported that the median concentration of molybdenum in 3,063 samples was 1.0 µg/L, with a maximum value of 4,700 µg/L (USGS 2011). Approximately 1.5% of the groundwater samples had molybdenum levels exceeding the health-based screening level of 40 µg/L (USGS 2011). Levels of molybdenum tended to be greatest in glacial unconsolidated sand and gravel aquifers as compared to other major aquifer groups in the study.

A report issued by the Wisconsin Department of Natural Resources found elevated levels of molybdenum in private supply wells and groundwater monitoring wells near the We Energies Oak Creek power plant

located in Caledonia, Wisconsin (WDNR 2013). Molybdenum levels in 21 private well samples exceeded the state of Wisconsin groundwater enforcement standard of 40 µg/L. It was not determined whether the elevated levels of molybdenum were naturally occurring or were a consequence of the activities of the power plant and the coal ash fill areas located nearby the plant.

In January of 2017, the EPA published the final results of the third Unregulated Contaminant Monitoring Rule (UCMR 3) program. Molybdenum levels >1 µg/L were measured in 25,377 out of 62,981 analyzed drinking water samples, and 151 samples had levels greater than the health-based screening level of 40 µg/L. In 40 of the 4,922 public water systems tested, at least one measurable level above 40 µg/L was found (EPA 2017b). Concentrations as high as 1,400 µg/L have been detected in drinking waters in areas impacted by mining and milling operations (USGS 2011).

In a study of finished drinking water supplies from the 100 largest cities in the United States in 1964, median and maximum molybdenum concentrations of 1.4 and 68 µg/L, respectively, were reported (USGS 1964). Another study reported a mean molybdenum concentration of 8 µg/L in samples collected from 161 drinking water sources from 44 states in the United States (Hadjimarkos 1967). Molybdenum levels measured onsite at 12 public water facilities across England and Wales ranged from below the detection limit (0.03 µg/L) to 1.51 µg/L over an 18-month collection period (Smedley et al. 2014). Corresponding molybdenum levels in tap water from 24 residences in three towns (North Wales, the English Midlands, and South East England) served by these public water facilities ranged from <0.03 to 1.00 µg/L. The study indicated that there was little variability in molybdenum concentrations when comparing levels in tap water versus respective water supply facilities, construction ages of the residences (i.e., new homes versus older homes), and pre-flush versus post-flush tap samples, suggesting that water distribution pipework has a negligible effect on supplied tap water levels of molybdenum.

Drinking water may also be affected by industrial contamination, as water treatment facilities are ineffective at removing molybdenum from source waters. In tap waters samples collected in 1971 from Golden, Colorado, a community that derives its water supply from a stream draining a molybdenum mine and mill, the mean molybdenum concentration was reported to be 440 µg/L. However, after the mine closed in 1974, the mean concentration in drinking water samples decreased to 150 µg/L by January 1975, 60 µg/L by June 1975, and 30 µg/L by 1977 (EPA 1979).

5.5.3 Sediment and Soil

Globally, most soils contain molybdenum at concentrations between 0.6 and 3.5 mg/kg, although total concentrations in soils can vary widely depending on geological composition, soil horizon, or industrial contamination. Statistical analysis of 4,841 samples of soil collected from a depth of 0–5 cm in the conterminous United States showed molybdenum levels ranging from <0.05 to 75.7 mg/kg (USGS 2014). The 5th, 25th, 50th, 75th, and 95th percentile concentrations were 0.24, 0.51, 0.78, 1.14, and 2.27 mg/kg, respectively (USGS 2014). From 4,780 samples of C horizon (substratum) soils in the United States, the molybdenum levels were reported as ranging from <0.05 to 94.7 mg/kg and the 5th, 25th, 50th, 75th, and 95th percentile concentrations were 0.20, 0.51, 0.83, 1.27, and 2.88 mg/kg, respectively (USGS 2014). A review of 25,673 deep soil samples from the British Geological Survey reported molybdenum concentrations of <0.6–885 mg/kg, with a median value of 1.4 mg/kg (Smedley and Kinniburgh 2017). The Forum of European Geological Surveys (FOREGS), under the International Union of Geological Sciences/International Association of Geochemistry (IUGS/IAGC) Global Geochemical Baselines Programme, collected 840 topsoil samples from 26 European countries and reported molybdenum concentrations ranging from <0.1 to 21.3 mg/kg (mean 0.943 mg/kg) (FOREGS 2005).

Above average molybdenum soil concentrations may occur in areas containing molybdenum-rich rock formations or in areas of industrial contamination. Natural sources sampled, including soils covering a mineralized area, soil derived from a marine black shale, alluvial soils on the eastern footslopes of Sierra Nevada, and soils formed from volcanic ash in Kauai, Hawaii, contained mean molybdenum concentrations of 76, 12, 17.4, and 14.9 mg/kg, respectively. Soils sampled near industrial contamination, such as soils downstream from a molybdenum mine and mill in Colorado, soil irrigated with water contaminated by a uranium mill, and soils 2 miles from a molybdenum smelter in Pennsylvania, had mean molybdenum concentrations of 59, 61, and 29 mg/kg, respectively (EPA 1979).

Typical molybdenum concentrations found in stream sediments were reported to range from 1 to 5 mg/kg (EPA 1979). Sediments in streams that drain water from natural deposits of molybdenum in the United States have been reported to have molybdenum concentrations ranging from 10 to 200 ppm (10–200 mg/kg). Another study reported molybdenum levels of up to 300 mg/kg in sediments derived from black marine shales in England. Stream sediment collected from water below a molybdenum mine and mill in Colorado had molybdenum concentrations ranging from 50 to 1,800 mg/kg (mean of 530 mg/kg). Molybdenum content in stream sediments have been shown to reflect mineralization, as the concentration increases with decreasing sediment grain size (EPA 1979). FOREGS collected 848 freshwater sediment

samples from 26 European countries and reported molybdenum concentrations ranging from 0.12 to 117 mg/kg (mean 1.34 mg/kg) (FOREGS 2005). An analysis of 65,477 stream sediments in the British Geological Survey G-Base reported a range of molybdenum concentrations of <0.1–309 mg/kg, with a median of 0.4 mg/kg (Smedley and Kinniburgh 2017). Sediment samples collected from river/streams in Tibet close in proximity to mining operations had molybdenum levels of 9.1–20.8 mg/kg (Huang et al. 2010).

5.5.4 Other Media

In a study detecting and comparing trace elements in the milk of guinea pigs (n=87), dairy cattle (n=48), horses (n=35), and humans (n=84), the average molybdenum concentrations measured were 26, 22, 16, and 17 µg/L, respectively (Anderson 1992). Average concentrations of molybdenum detected in six kinds of milk, including cow's milk-based formula, breast milk, soya milk, bottled milk, dried milk, and evaporated milk, were 18, 4, 160, 34, 35, and 29 µg/L, respectively (Biego et al. 1998). Most of the molybdenum is in the cream fraction (Archibald 1951).

Food derived from aboveground plants, such as legumes, leafy vegetables, and cauliflower generally has a relatively higher concentration of molybdenum in comparison to food from tubers or animals. Beans, cereal grains, leafy vegetables, legumes, liver, and milk are reported as the richest sources of molybdenum in the average diet (Barceloux 1999).

Typical concentrations of molybdenum in plants are 1–2 mg/kg; however, a range of tenths to hundreds of mg/kg have been reported (EPA 1979). Tobacco contains molybdenum concentrations of 0.3–1.76 mg/kg (Barceloux 1999).

5.6 GENERAL POPULATION EXPOSURE

Molybdenum exposure to the general population via ambient air and drinking water is expected to be negligible compared with exposure through food (Barceloux 1999). Molybdenum does not occur naturally in the pure metallic form. It is principally found as oxide or sulfide compounds (Barceloux 1999; EPA 1979). Therefore, almost all exposure is to a molybdenum compound rather than the metal alone. The average dietary intake of molybdenum in the United States by adult men and women are 109 and 76 µg/day, respectively (NAS 2001). A study of the dietary intake of adult residents in Denver, Colorado reported a mean molybdenum ingestion rate of 180 µg/day (range 120–240 µg/day) (Barceloux

1999). Daily intakes ranged from 74 to 126 µg molybdenum in a study of older children and adults in the northeastern United States (Barceloux 1999).

The European Food Safety Authority (EFSA) used dietary intake studies to derive estimates of which foods were most responsible for molybdenum intake in European populations (EFSA 2013). Cereals and cereal-based products (including bread) are the largest contributors to molybdenum intake in a Western diet; these products contribute one-third to one-half of the total molybdenum intake. Other contributors to total molybdenum intake include dairy products and vegetables.

A summary of molybdenum concentrations positively identified in foods analyzed during the FDA Total Diet Study (TDS) of 2006–2011 and 2013–2014 is summarized in Table 5-8 (FDA 2017). The data for molybdenum arose from Market Basket Surveys conducted in 2010 and 2011 and 2013–2014, in which 382 store-bought foods purchased in four geographic regions of the United States (northeast, southeast, central, and west) were analyzed. Only those food items in which the molybdenum content of at least one sample was above the detection limit of the analytical method are reported. Another survey of levels of molybdenum in food found the highest molybdenum concentrations in legumes; grains and grain products; nuts; meat, fish, and poultry (including liver); eggs; and milk, yogurt, and cheese (76.7, 30.0, 29.5, 8.9, 6.3, and 4.6 µg/100 g, respectively) (Pennington and Jones 1987).

Table 5-8. Molybdenum Levels Detected in Foods in the 2006–2011 and 2013–2014 Market Basket Surveys[a]

Food	Number of samples	Positive detections	Mean (mg/kg)	Median (mg/kg)	Maximum (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)
Liver (beef/calf), pan-cooked with oil	8	8	1.500	1.400	1.700	0.700	3.000
Pinto beans, dry, boiled	8	8	1.300	1.270	1.600	0.700	3.000
Pork and beans, canned	8	1	0.088	0	0.700	0.700	3.000
Peanut butter, smooth/creamy	8	3	0.508	0	1.900	0.900	3.000
Shredded wheat cereal	8	5	0.554	0.883	0.984	0.700	3.000
Raisin bran cereal	8	1	0.088	0	0.701	0.700	3.000
Crisped rice cereal	8	8	0.898	0.837	11.300	0.700	3.000
Granola with raisins	8	6	0.589	0.772	0.815	0.700	3.000
Oat ring cereal	8	8	1.300	1.300	1.400	0.700	3.000
Collards, fresh/frozen, boiled	8	2	0.262	0	1.600	0.500	2.000
Chili con carne with beans, canned	8	2	0.179	0	0.730	0.700	3.000
Refried beans, canned	8	2	0.254	0	1.100	0.800	3.000

Table 5-8. Molybdenum Levels Detected in Foods in the 2006–2011 and 2013–2014 Market Basket Surveys[a]

Food	Number of samples	Positive detections	Mean (mg/kg)	Median (mg/kg)	Maximum (mg/kg)	LOD (mg/kg)	LOQ (mg/kg)
White beans, dry, boiled	8	8	1.100	1.116	1.800	0.700	3.000
Granola bar, with raisins	8	1	0.164	0	1.300	0.800	3.000
Candy bar, chocolate, nougat, and nuts	8	1	0.115	0	0.922	0.800	3.000

[a]Trace values were defined as results ≥LOD and <LOQ. Results ≥LOD and <LOQ (trace values) were used as reported when calculating the means.

LOD = limit of detection; LOQ = limit of quantification

Source: FDA 2017 (Data were initially released in 2014 and revised April 2017.)

Molybdenum is an essential dietary element and is often included in nutritional supplements. Based on data from NHANES, the median molybdenum intake from dietary supplements was about 23 and 24 µg/day for men and women who reported supplement use, respectively. Dietary supplements generally contain molybdenum in the form of sodium molybdate or ammonium molybdate (Momcilovic 1999; NAS 2001), although the molybdenum can also be in the form of molybdenum chloride, molybdenum glycinate, and molybdenum amino acid chelate (NIH 2019).

It was reported in 1979 that in the United States, the average human intake of molybdenum via drinking water was <5 µg/day (EPA 1979). Drinking water coming from sources close to areas with high molybdenum contamination from industrial effluents may contain a higher concentration of molybdenum (>50 µg/L) (EPA 1979).

Urinary levels of molybdenum were measured for the U.S. population from NHANES studies from 1999 to 2016 (CDC 2019) and are summarized in Table 5-9.

Table 5-9. Urinary Molybdenum Levels in U.S. Adults

Survey years	Geometric mean	50th percentile	95th percentile	Sample size
		Urinary molybdenum (µg/L)[a]		
1999–2000	41.7 (36.7–47.4)	46.6 (40.5–52.5)	168 (143–206)	1,299
2001–2002	41.1 (38.3–44.1)	47.6 (43.7–51.2)	150 (130–166)	1,560
2003–2004	35.9 (34.0–38.0)	40.3 (37.6–42.1)	133 (119–144)	1,543
2005–2006	41.3 (38.7–44.0)	46.0 (41.7–49.6)	153 (135–171)	1,520
2007–2008	40.8 (38.7–43.0)	44.5 (42.2–47.8)	152 (145–164)	1,857

Table 5-9. Urinary Molybdenum Levels in U.S. Adults

Survey years	Geometric mean	50th percentile	95th percentile	Sample size
2009–2010	39.6 (37.5–41.8)	42.0 (39.8–43.9)	144 (130–163)	2,019
2011–2012	34.1 (31.8–36.5)	37.3 (33.6–39.8)	136 (120–146)	1,715
2013–2014	30.8 (28.58–33.3)	32.7 (28.3–36.0)	129 (116–137)	1,811
2015–2016	32.0 (29.9–34.1)	35.9 (33.1–37.8)	124 (112–136)	1,793
Creatinine corrected urinary molybdenum (µg/g creatinine)				
1999–2000	39.6 (36.9–42.6)	38.5 (36.1–41.0)	122 (116–147)	1,299
2001–2002	39.3 (36.8–42.0)	39.6 (36.4–42.1)	123 (109–139)	1,559
2003–2004	36.9 (35.0–38.9)	37.0 (35.7–38.4)	118 (101–134)	1,543
2005–2006	41.2 (39.3–43.1)	40.5 (38.8–42.7)	119 (103–132)	1,520
2007–2008	43.5 (42.1–44.9)	42.9 (41.3–44.7)	122 (110–132)	1,857
2009–2010	41.9 (40.0–43.9)	41.2 (39.4–43.0)	127 (115–141)	2,019
2011–2012	38.6 (37.5–42.2)	40.0 (36.0–43.6)	118 (108–131)	1,261
2013–2014	35.9 (33.7–38.2)	36.9 (35.1–38.4)	97.8 (88.5–111)	1,810
2015–2016	34.9 (33.3–36.6)	36.3 (34.4–38.1)	97.4 (85.5–102)	1,791

[a]Limit of detection for survey years 1999–2001, 2001–2002, 2003–2004, 2005–2006, 2007–2008, 2009–2010, 2011–2012, 2013–2014, 2015–2016 were 0.8, 0.8, 1.5, 0.92, 0.92, 0.99, 0.8, and 0.8 µg/L, respectively.

Source: CDC 2019

Paschal et al. (1998) analyzed the levels of molybdenum and 12 other metals in the urine of 496 residents of the United States obtained from the NHANES III survey conducted from 1988 to 1994. The specimens randomly selected were from a broad spectrum of the population (e.g., both urban and rural communities, both males and females, and persons aged 6–88 years from all major ethnicities). The geometric mean molybdenum concentration of the samples was 46.8 µg/L and the 25th, 50th, 75th, and 95th percentiles were 27.9, 56.5, 93.9, and 168.0, µg/L, respectively. The creatinine-adjusted 25th, 50th, 75th, and 95th percentiles were 30.9, 45.7, 64.3, and 133.8 µg/g, respectively, with a geometric mean of 39.6 µg/g.

Molybdenum levels in whole blood are typically <5 ng/mL in the general population; however, blood samples from persons from areas with natural molybdenum deposits or from molybdenum mining areas may have concentrations of up to 150 µg/mL (Barceloux 1999).

Blood samples collected from 18 miners at a molybdenum mine in New Mexico had plasma molybdenum levels <5 µg/L in 12 of the 18 samples and 6–18 µg/L in the remaining 6 samples. The concentration of molybdenum in urine collected from 11 of the miners ranged from 20 to 74 µg/L. It was noted that

molybdenum levels in urine and blood of miners mainly exposed to molybdenite may not be above average, since molybdenite is a relatively insoluble compound (EPA 1979).

In a survey of a molybdenite mining, crushing, and milling operation in Colorado, mean molybdenum levels in respirable dust samples were 0.471, 1.318, 0.142, and 0.318 mg/m^3 during mining, crushing, milling, and open pit operations, respectively (EPA 1979). In settled dust and air samples collected from a molybdenum smelting operation, concentrations of molybdenum, in the form of molybdenum trioxide, were 57–61% and 3–33 mg/m^3, respectively (EPA 1979). Forty air samples collected above a crucible in a molybdenum trioxide smelting plant contained a mean molybdenum concentration of 0.22 mg/m^3, while air samples collected in the breathing zone of workers had molybdenum concentrations ranging from 1.4 to 5.4 mg/m^3 (EPA 1979). The air concentrations of molybdenum in two plants that produce molybdenum salts were 0.5–200 and 0.2–30 mg/m^3 (EPA 1979). More recent monitoring data for mining and milling operations were not located; current levels may be lower due to possible changes in occupational standards, engineering and administrative controls, and personal protective equipment requirements.

Workers involved in metal refining and metal working may be exposed to airborne particulates containing molybdenum. In a study assessing the exposure of a group of 20 workers performing welding, polishing, and assembly of stainless steel constructions, molybdenum was detected in personal air samplers at concentrations of 0.27–9.7, 0.03–4.2, and 0.14–0.60 µg/m^3, respectively. Stationary air samplers in the facility detected course (equivalent aerodynamic diameter [EAD] 2–10 µm) and fine (EAD <2 µm) molybdenum particles at concentrations of 0.015–0.087 and 0.093–0.54 µg/m^3, respectively (Kucera et al. 2000).

The National Occupational Exposure Survey (NOES) conducted by NIOSH in 1983 estimated that 245,024 workers employed at 15,996 facilities were potentially exposed to molybdenum (pure, powder, and unknown forms) in the United States (RTECS 2009). The NOES database does not contain information on the frequency, concentration, or duration of exposure; the survey provides only estimates of workers potentially exposed to chemicals in the workplace.

The extensive nationwide use of radioactive ^{99}Mo in generators that produce ^{99m}Tc for nuclear medicine imaging scans can expose medical staff and the public in medical facilities to low levels of ionizing radiation. The extent of those exposures is limited by the USNRC and agreement state regulations (USNRC 2016a, 2016b).

Breast milk and infant formula are the primary sources of molybdenum in infants aged 0–6 months (NAS 2001). The primary source of dietary molybdenum intake among children in the United States is milk (EPA 1979). Several studies have measured molybdenum levels in human breast milk; average molybdenum levels ranged from 1.5 to 17 µg/L (Anderson 1992; Aquilio et al. 1996; Biego et al. 1998; Bougle et al. 1988). As shown in Table 5-10, the highest molybdenum concentrations occur within the first week after birth and tend to be higher in the mothers of term infants, as compared to preterm infants (Aquilio et al. 1996; Bougle et al. 1988).

Table 5-10. Molybdenum Levels in Breast Milk in Mothers of Term and Preterm Infants

	Molybdenum levels in breast milk (µg/L)		
Lactation day	Term infants	Preterm infants	Reference
2–6	6.8	3.9[a]	Aquilio et al. 1996
12–16[b]	5.7	2.4[a]	
21[c]	3.6	1.9[a]	
3–5	10.2	4.0[a]	Bougle et al. 1988
7–10[d]	4.8	3.7	
14[d]	1.5	1.4	
30[d]	2.6	1.9	
60[e]	No data	1.2	

[a]Significantly different from term infant levels ($p<0.05$).
[b]Significantly different from molybdenum concentration at 2-6 days ($p<0.01$).
[c]Significantly different from molybdenum concentration at 2-6 days ($p<0.05$).
[d]Significantly different from molybdenum concentration for whole group at 3-5 days ($p<0.01$).
[e]Significantly different from molybdenum concentration at for whole group at 3-5 days ($p<0.05$).

Krachler and colleagues studied the trace element concentrations in human milk during the course of lactation (Krachler et al. 1998; Rossipal and Krachler 1998). In total, 79 samples of human milk from 46 healthy mothers were sampled in Austria in 1995 and 1996 at 1–293 days after the mothers gave birth (Rossipal and Krachler 1998). In colostrum milk (1–3 days postpartum), the molybdenum concentration was 8.88±3.74 µg/L. In samples collected 42–60 days postpartum, the concentration was 1.43±1.77 µg/L, and at 97–293 days, the milk contained 1.78±1.62 µg/L. In a later study, the same group analyzed a further set of samples of colostrum milk only (Krachler et al. 1999). Previous results were confirmed, with the mean concentration being reported as 7.0±3.8 µg/L (median 5.7 µg/L, range 3.4–18.8 µg/L). Another study from Europe reported molybdenum concentrations in human milk (Wappelhorst et al. 2002). In samples taken daily in 2002 from 19 mothers from Germany, Poland, and

the Czech Republic, for sample periods between 2 and 8 weeks for each mother and covering weeks 3–68 of lactation, the median molybdenum concentration was 0.53 µg/L (mean 0.72 µg/L, range 0.27–1.61 µg/L). Data on molybdenum concentrations in human milk are also available from Japan (Hattori et al. 2004). In 17 samples provided by three mothers during days 96 and 327 after delivery, the molybdenum concentrations ranged from 1.97 to 8.93 µg/L, with an estimated average of ~4.3 µg/L (estimated from three median values given for the individual mothers). In comparison, the concentration of molybdenum in formula milk after preparation is reported as 2.38±0.75 µg/L (n=6). In Canada, 20 samples of mother's milk were analyzed for molybdenum in the context of a balance study on low-birth-weight infants on parenteral and enteral nutrition (Friel et al. 1999b). The median molybdenum concentration is reported as 5 µg/L, with a range of 2.1–23 µg/L.

Urinary levels of molybdenum in children 6–11 and 12–19 years old were measured during the NHANES study assessing exposure from 1999 to 2016 (CDC 2019) and in children 3–5 years of age during NHANES 2015–2016; these data are summarized in Table 5-11.

Table 5-11. Urinary Molybdenum Levels in U.S. Children and Adolescents

Survey years	Geometric mean	50th percentile	95th percentile	Sample size
	Urinary molybdenum (µg/L)[a]			
1999–2000				
Age 6–11 years	78.2 (61.0–100)	84.8 (67.7–105)	267 (159–840)	310
Age 12–19 years	54.3 (47.6–62.0)	60.6 (52.2–70.3)	188 (146–216)	648
2001–2002				
Age 6–11 years	63.3 (53.4–75.0)	69.2 (63.0–77.6)	197 (161–291)	368
Age 12–19 years	60.6 (55.5–66.2)	65.7 (58.7–73.1)	179 (155–227)	762
2003–2004				
Age 6–11 years	62.2 (56.7–68.3)	71.3 (55.7–84.1)	181 (138–235)	290
Age 12–19 years	52.5 (49.0–56.3)	59.6 (55.5–65.1)	143 (130–156)	725
2005–2006				
Age 6–11 years	65.6 (56.6–76.0)	73.5 (62.8–85.5)	181(154–205)	355
Age 12–19 years	59.1 (53.7–65.1)	63.8 (57.9–69.4)	173 (148–202)	701
2007–2008				
Age 6–11 years	69.3 (60.8–79.0)	72.8 (62.1–83.9)	235 (169–282)	394
Age 12–19 years	64.1 (58.6–70.2)	68.6 (63.7–80.2)	174 (151–196)	376
2009–2010				
Age 6–11 years	65.0 (57.8–73.2)	69.7 (61.1–84.2)	218 (180–263)	378
Age 12–19 years	52.4 (47.5–57.7)	58.5 (51.4–65.6)	178 (151–201)	451

Table 5-11. Urinary Molybdenum Levels in U.S. Children and Adolescents

Survey years	Geometric mean	50th percentile	95th percentile	Sample size
2011–2012				
Age 6–11 years	58.4 (51.5–66.2)	65.1 (52.8–74.5)	211 (187–283)	399
Age 12–19 years	46.4 (40.2–53.7)	51.0 (44.2–64.8)	163 (145–173)	390
2013–2014				
Age 6–11 years	51.7 (47.1–56.6)	54.7 (49.3–61.9)	182 (159–210)	402
Age 12–19 years	48.2 (41.5–55.8)	55.9 (49.0–64.8)	156 (136–180)	451
2015–2016				
Age 3–5 years	47.3 (43.9–50.8)	51.6 (45.8–61.1)	191 (146–218)	486
Age 6–11 years	56.2 (51.3–61.5)	57.5 (50.2–69.1)	173(165–224)	379
Age 12–19 years	47.7 (43.3–52.6)	53.0 (45.9–57.0)	149 (135–166)	402
Creatinine corrected urinary molybdenum (µg/g creatinine)				
1999–2000				
Age 6–11 years	85.9 (73.7–100)	79.3 (71.6–88.4)	214 (154–1,040)	310
Age 12–19 years	41.9 (39.3–44.6)	40.5 (37.7–44.4)	112 (78.4–185)	648
2001–2002				
Age 6–11 years	77.2 (73.1–81.5)	77.6 (71.8–84.5)	185 (165–219)	368
Age 12–19 years	43.4 (40.8–46.1)	44.1 (40.8–47.2)	106 (94.8–118)	762
2003–2004				
Age 6–11 years	72.5 (65.2–80.7)	73.5 (65.1–79.9)	160 (129–257)	290
Age 12–19 years	37.5 (35.4–39.8)	38.9 (36.9–41.8)	81.0 (74.3–102)	725
2005–2006				
Age 6–11 years	81.0 (71.9–91.3)	78.6 (72.1–89.0)	201(160–261)	355
Age 12–19 years	45.5 (42.5–48.7)	45.7 (41.3–49.2)	109 (95.0–131)	701
2007–2008				
Age 6–11 years	90.4 (81.8–99.8)	88.2 (79.2–101)	274 (224–354)	394
Age 12–19 years	50.1 (47.2–53.2)	50.1 (44.2–53.4)	129 (99.5–138)	376
2009–2010				
Age 6–11 years	88.6 (81.9–95.4)	89.0 (79.2–95.4)	195 (178–216)	378
Age 12–19 years	49.0 (45.3–53.0)	50.7 (44.6–56.2)	126 (96.4–134)	451
2011–2012				
Age 6–11 years	83.5 (76.1–91.6)	81.7 (74.3–91.2)	259 (185–300)	398
Age 12–19 years	44.4 (40.8–48.4)	43.7 (39.1–48.0)	109 (92.4–131)	390
2013–2014				
Age 6–11 years	77.0 (73.5–80.8)	73.5 (70.0–81.4)	184 (164–225)	402
Age 12–19 years	43.6 (40.3–47.2)	44.0 (39.1–47.3)	113 (95.9–140)	451

Table 5-11. Urinary Molybdenum Levels in U.S. Children and Adolescents

Survey years	Geometric mean	50th percentile	95th percentile	Sample size
2015–2016				
Age 3–5 years	109 (102–116)	107 (98.4–117)	275 (239–329)	485
Age 6–11 years	79.7 (75.5–84.1)	79.6 (69.9–86.7)	200(171–229)	379
Age 12–19 years	44.6 (41.9–47.5)	45.0 (41.8–48.7)	107 (89.3–133)	402

[a]Limit of detection for survey years 1999–2001, 2001–2002, 2003–2004, 2005–2006, 2007–2008, 2009–2010, 2011–2012, 2013–2014, 2015–2016 were 0.8, 0.8, 1.5, 0.92, 0.92, 0.99, 0.8, and 0.8 µg/L, respectively.

NHANES = National Health and Nutrition Examination Survey

Source: CDC 2019; NHANES data are periodically updated, and the most recent information can be found at https://cdc.gov/exposurereport/index.html.

5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

Workers in an industrial setting such as mining, metal refining, and metal working can be exposed to significant levels of molybdenum (Kucera et al. 2000). Populations living close to areas with high molybdenum contamination from industrial effluents and high mineral deposits are at risk for higher exposures (EPA 1979).

^{99}Mo generators are the major source of ionizing radiation exposure to nuclear medicine staff in medical facilities that perform ^{99m}Tc diagnostic imaging scans (Ahasan 2004).