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Chemical Constituents in Coal Combustion Products: Molybdenum

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Chemical Constituents in Coal Combustion Products: Molybdenum

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REPORT SUMMARY

This report provides comprehensive information on the environmental occurrence and behavior of molybdenum (Mo), with specific emphasis on Mo derived from coal combustion products (CCPs). Included are discussions of Mo's occurrence in water and soil, potential human health and ecological effects, geochemistry, occurrence in CCPs, leaching characteristics from CCPs, measurement techniques, and treatment/remediation options.

Background

Mo is a metal that naturally occurs in air, water, soil, and coal. Due to its presence in coal, coal-fired power plants produce CCPs containing Mo as a byproduct of electricity generation. Mo has the capacity to leach from coal ash when stored, and it has relatively high mobility in groundwater. Although the United States Environmental Protection Agency (US EPA) has not established a maximum contaminant level for Mo in water, nonenforceable standards have been developed for water and soil. To manage CCP sites effectively, it is important to understand available information regarding Mo's leaching potential, environmental behavior, and concentrations in various media, as well as the exposure levels associated with adverse human and ecological effects.

Objective

- To assemble and synthesize information on molybdenum with respect to the environmental occurrence, environmental behavior, and potential human health effects, with specific emphasis on the implications for CCP management

Approach

The project team performed a literature search using several databases, focusing on environmental data and human health information, in order to compile relevant information on Mo. Key secondary research sources and relevant EPRI reports and data were also collected and reviewed. Information from these sources was summarized so that key data and references could be contained and accessed easily in one report.

Results

Mo occurs at relatively low levels in soil and water. Worldwide concentrations of Mo in soils vary from about 0.1 to 10 mg/kg, with an average concentration of approximately 1–2 mg/kg. Mo concentrations are typically around 1 μg/L in fresh surface water and up to 10 μg/L in groundwater. Mo concentrations in coal are similar to concentrations in soil; Mo is enriched in CCPs, with mean concentrations around 10–20 mg/kg.

Mo is an essential element that is necessary for optimal health. Because of this, the Institute of Medicine (IOM) of the National Academy of Sciences (NAS) has established a recommended dietary allowance (RDA) for Mo of 34–45 μg/day for nonpregnant adults. Although Mo at low levels is necessary for optimal health, Mo can also be associated with adverse effects via oral exposure at higher concentrations. The most common and sensitive health effects observed are increased uric acid production and gout. Based on these endpoints and a margin of safety, the EPA has established a reference dose for Mo of 0.005 mg/kg-day. This is lower than the tolerable upper intake level developed by IOM of 0.03 mg/kg-day. The EPA also determined that the information available to evaluate Mo's carcinogenic potential in humans or animals is inadequate.

Molybdate is the principal form of Mo that is encountered in oxic waters. Molybdate has relatively high mobility in groundwater, with distribution coefficient values ranging from 0.6 to 501 L/kg. Mo adsorption on both minerals and organic matter is highly pH dependent, with peak adsorption at pH < 5 and limited adsorption above a pH of 8.

Mo is typically present in CCP leachate at concentrations from about 0.25 up to a few mg/L. The highest Mo concentrations at CCP disposal sites are associated with fly ash in landfills; the lowest are associated with flue gas desulphurization gypsum. The leaching behavior of Mo from CCPs depends on several factors, including pH, CCP composition, and the CCP weathering state.

The most viable remediation technologies for the treatment of aqueous Mo are adsorption and chemical precipitation, although biological treatment and membrane filtration are promising—but not yet proven—remediation techniques. Both *ex situ* (using conventional "pump-and-treat") and *in situ* (using permeable reactive barriers and subsurface injection) methods can be used to remediate Mo. As with most metals, pH control is an important consideration for Mo remediation.

Keywords

Coal combustion products
Ecological effects
Geochemistry
Human health
Leachate
Molybdenum

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INTRODUCTION

Coal combustion products (CCPs), which are produced when coal is burned to generate electricity, contain a variety of trace metals. Characterizing the potential human health, ecological, and environmental risks that can result from the management of CCPs has been an important research topic for the Electric Power Research Institute (EPRI) and federal regulatory agencies, such as the United States Environmental Protection Agency (US EPA), for several decades. These issues have gained heightened attention in recent years, and US EPA is currently proposing changes to the regulation of CCP disposal practices.

Because CCPs disposed of in landfills and surface impoundments have the potential to impact surface water, groundwater, soil, and sediment, it is important to have a complete understanding of the key constituents in CCPs. In particular, it is important to understand the leaching behavior of these constituents under different environmental conditions and the environmental levels of these constituents that may lead to potential exposures and adverse human health and ecological effects.

Molybdenum (Mo) is one of the trace elements present in CCPs. While less studied than some other trace elements in CCPs (*e.g.*, arsenic, selenium, mercury), Mo can pose an environmental concern if CCPs are managed improperly. In fact, the recent US EPA human health and ecological risk assessment of CCPs determined that Mo could pose a potential human health risk (US EPA, 2010a). While US EPA's analysis was hypothetical and relied on a considerable number of conservative assumptions and simplifications (particularly with regard to metal fate and transport), the risk assessment findings underscore the importance of understanding the potential for Mo to leach from waste management units, and whether those releases are at levels that can impact human and ecological receptors, under more realistic, real-world conditions.

This report describes the current understanding of Mo occurrence and behavior in the environment as well as in CCPs and CCP-related waste streams. Mo concentrations in various media, as well as in CCPs, are summarized in Chapter 2. In Chapters 3 and 4, the potential health and ecological impacts are discussed. Chapter 5 covers the fate and transport of Mo, and Chapter 6 addresses CCP leaching behavior specifically. Sampling and analyses related to Mo are discussed in Chapter 7. Lastly, Chapter 8 discusses treatment and remediation options.

2

OCCURRENCE, USES, AND SOURCES

2.1 Occurrence and Forms

Molybdenum (Mo) is a naturally occurring transition metal that can be found in the environment in several different valence states; the most common valence states for naturally occurring Mo are Mo (+4) and Mo (+6). In the Mo (+4) valence state, Mo is usually complexed with sulfur to form the compound molybdenite (MoS_2). Not only is molybdenite the most abundant form of Mo in ores, but it is also the most commercially valuable form. Other common Mo minerals include a lead complex called wulfenite ($PbMoO_4$) and a calcium complex called powellite ($CaMoO_4$). In soil, Mo is generally found adsorbed to iron or aluminum oxides, clay, and/or organic matter. In water, the Mo (+6) valence (molybdate ion, MoO_4^{2-}) dominates Mo aqueous speciation except under low pH (< 4) and anoxic conditions. In Chapter 5, Mo chemical and physical properties are described in more detail.

Table 2-1
Typical Molybdenum Concentrations in Environmental Media

Environmental Media		Concentration Mean/*Median*[1] (Min-Max)	Reference
US soil (mg/kg)		1.0 / *0.77* (0.08-21)	EPRI, 2010
Rocks and minerals (mg/kg)		*1.6* (< 0.05-640)	EPRI, 2010
Water (µg/L)	Surface freshwater	68[2] (4-1100)	Hem, 1985
	Groundwater	20 / *9* (4-5292)	USGS, 2011
	Drinking water supplies	*1.4* (ND[3]-68 µg/L)	WHO, 2003
Atmosphere (µg/m^3)	Rural areas	(0.0001-0.003)	Eisler, 1989
	Urban areas	(0.01-0.03)	Eisler, 1989
US coal (mg/kg)		*1.7* (0.03-280)	USGS, 1998a
CCPs (mg/kg)		19.2 / *11.2* (0.04-236)	EPRI, 2011a
CCP leachate (mg/L)		1.1 / *0.25* (< 0.1-60.8)	EPRI, 2011a

Notes: *[1] The central tendency estimate was reported as a mean or median (in italics), depending on the reference source.*
[2] Based on one-third of the data which was above the detection level (thus, this reported mean is skewed high).
[3] ND = not detected.

2.1.1 Soil

Mo is the least abundant of the biologically essential trace elements in soil. The mean concentration of Mo in the upper continental crust, from which soil is formed, is 1.4 mg/kg (Wedepohl, 1995). Typical concentrations in soil, rocks, and minerals are listed in Table 2-1 and shown in Figure 2-1. Worldwide concentrations of Mo in soils vary from about 0.1-10 mg/kg, with an average concentration of about 1-2 mg/kg (Eisler, 1989, p. 8; US EPA, 1979, p. 31). Recent surveys in the US have reported average concentrations of about 1 mg/kg and median levels of 0.77 mg/kg, with a range of 0.08-21 mg/kg (EPRI, 2010, Table 4-1). Soils in highly mineralized areas have reported Mo concentrations ranging from 27-190 ppm (US EPA, 1979, p. 32). In addition, soil irrigated with effluent from a uranium mill in Colorado was found to contain as much as 72 mg/kg Mo (Eisler, 1989).

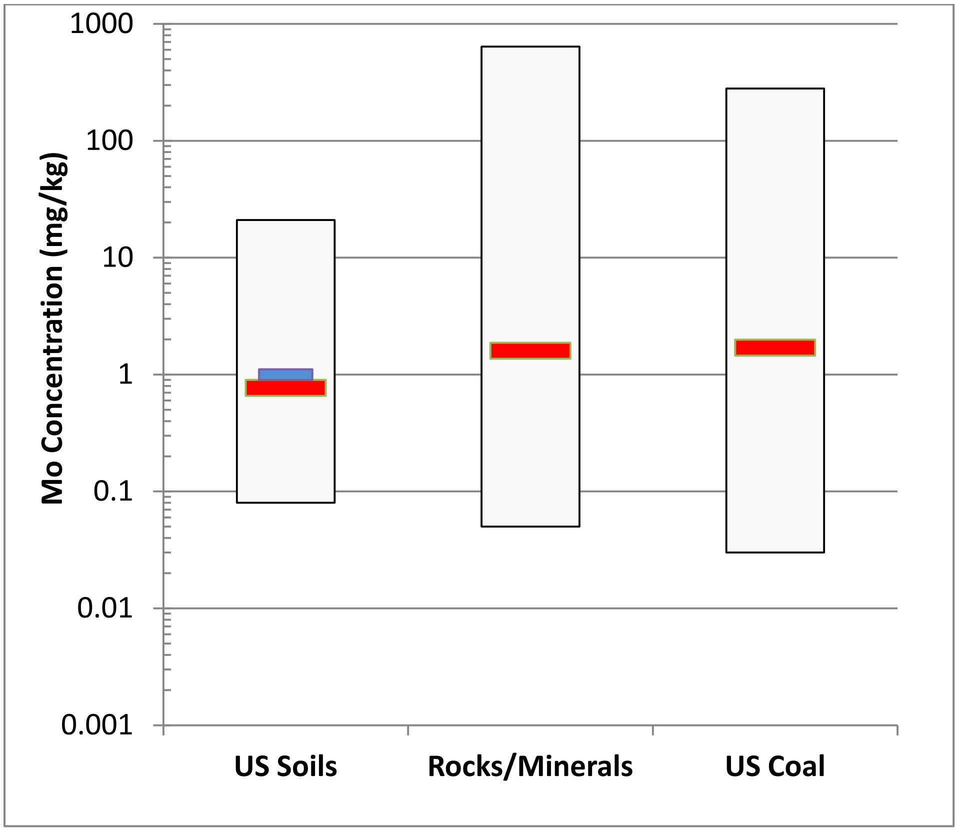

Figure 2-1
Comparison of Molybdenum Concentration in US Soils, Rocks and Minerals, and US Coal

Notes: Red lines indicate median concentration, blue lines indicate mean concentration.

Source: US Soils, Rocks and Minerals: EPRI, 2010; US Coal: USGS, 1998a.

2.1.2 Water

There is a wide range of concentrations of naturally occurring Mo in water. Typical Mo concentrations in water are listed in Table 2-1 and shown in Figure 2-2. Fresh surface waters are reported to typically contain approximately 1 µg/L Mo, while the Mo concentration in oxic seawater is reported to be approximately 10 µg/L (Ryzhenko, 2010; Bertine and Turekian, 1973).

Background concentrations of Mo in groundwater are on the order of 1-10 µg/L, but increase with alkalinity, reaching up to hundreds of µg/L (Ryzhenko, 2010).

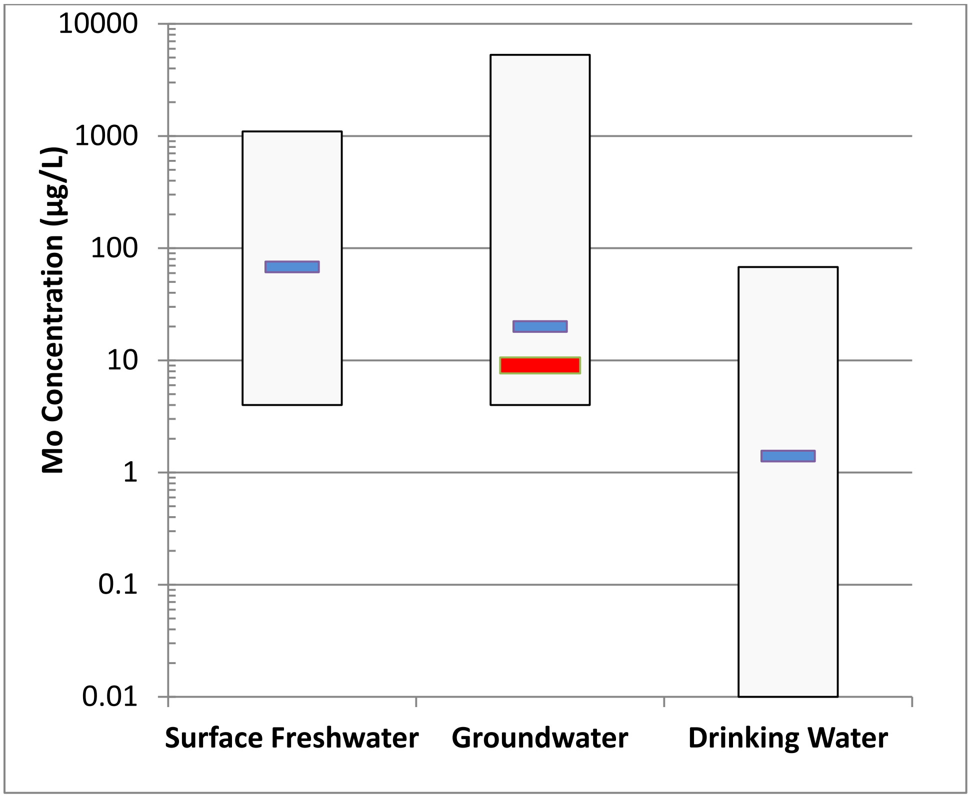

Figure 2-2
Range of Molybdenum Concentrations

Notes: Red lines indicate median concentration, blue lines indicate mean concentration.

Mean surface freshwater concentrations are skewed high, as they represent only the one-third of samples that were above detectable levels.

Sources: Surface freshwater: Hem, 1985; groundwater: USGS, 2011; drinking water: WHO, 2003.

As reviewed in the World Health Organization's (WHO's) background document for development of its drinking-water quality guidelines, surveys of Mo in water supplies were conducted in the US, although these data are quite dated (WHO, 2003). For example, in a 1967 survey, 32.7% of surface water samples from 15 major river basins had detectable levels of Mo, with concentrations ranging from 2-1500 µg/L and a mean for detected samples of 60 µg/L. Similarly, Koop and Kroner (1968, as cited in Hem, 1985) reported Mo concentrations for 1,500 stream water samples from 130 locations that were detectable in only one-third of the samples (detection levels ranged from 3-5 µg/L). The mean of the detectable samples was 68 µg/L (Koop and Kroner, 1968, cited in Hem, 1985).

In a survey of groundwater conducted in 1944, Mo levels ranged from non-detectable to 270 µg/L, with no mean/median reported (WHO, 2003). Treated water supplies were reported in a 1964 survey to have lower Mo concentrations, ranging from non-detectable to 68 µg/L, with a median of 1.4 µg/L (WHO, 2003). More recently, data available from the state of Minnesota reported a median concentration of Mo in groundwater monitoring wells of < 4.2 µg/L (MPCA, 1999). Data from Wisconsin showed that only 20% of the 2,700 water supply wells tested had detectable levels of Mo. The median of the detected concentrations was 4 µg/L, with 95% of wells containing < 11 µg/L. The highest level measured was 3,499 µg/L, but there was no information on whether this maximum concentration was due to a specific source of contamination (WDHSD, 2010). In North American rivers and lakes, Mo concentrations generally range from 0.4-4.1 µg/L, with > 100-10,000 µg/L in surface water associated with mining activities (Eisler, 1989).

2.1.3 Air

Environmental concentrations of Mo in air are generally low and constitute a minor pathway of exposure for the general population. Overall, surveys show that Mo concentrations in air range from 0.0001-0.003 µg/m^3 in rural environments and 0.01-0.03 µg/m^3 in urban environments in the US (Friberg *et al*., 1975, and Friberg and Lener, 1986, as cited in Eisler, 1989). In 1961, reported atmospheric concentrations of Mo in the United Kingdom (UK) in rural areas ranged from 0.00029-0.00129 µg/m^3 and from 0.00057-0.00700 µg/m^3 in a steelworks area (as cited in Chappell and Peterson, 1977, p. 362). Air concentrations of Mo in the vicinity of Mo-related industrial activities (*i.e.*, areas of active mining) and in occupational settings (*e.g.*, smelters) can be much higher. In a 1975 study of respirable Mo in dust, concentrations as high as 6 mg/m^3 were measured during ore crushing operations. Smelting operations can also result in similarly elevated occupational exposures to Mo via air (Chappell and Peterson, 1977).

2.1.4 Diet

Mo is an essential nutrient for humans; the recommended daily intake is 45 µg/day for adult men and women (IOM, 2001). Mo is readily taken up by a variety of plants and, as a result, plants are the major source of Mo in the human diet. In particular, legumes, grain products, and nuts are rich sources of Mo in the human diet (Pennington and Jones, 1987, Tsongas *et al*., 1980, as cited in IOM, 2001). A limited amount of information is available on typical Mo intake in the human diet. In a 1980 US study, Mo concentrations were reported to range from 120-240 µg/day, with an average intake of 180 µg/day (Tsongas *et al*., 1980, as cited in IOM, 2001). In 1987, the US Food and Drug Administration (US FDA) reported an average Mo intake of 76 µg/day for women and 109 µg/day for men (Pennington and Jones, 1987, as cited in IOM, 2001). These intakes are well above the recommended daily intake of 45 µg/day.

2.2 Uses

The chemical properties of Mo, namely its high melting temperature (*i.e.*, it has the sixth-highest melting temperature of all elements) and high thermal and electrical conductivity in the absence of thermal expansion, make it a commonly used material in manufacturing. US mines produced 56,000 tons of Mo in 2010; this is approximately one-quarter of 2010 total world production (USGS, 2011). About 75% of mined Mo is used as a component in stainless steel, other steel products, and cast iron. Mo is also used in superalloys, electronics, spark plugs, X-ray tubes, filaments, screens, and grids for radio valves, and in the production of tungsten, glass-to-metal seals, nonferrous alloys, and pigments. Mo disulfide is also widely used as a lubricant additive for machines and engines (IMOA, 2010a; WHO, 2003).

Mo is an essential nutrient for both plants and animals and, thus, it is added to some fertilizers and even sold as a dietary supplement. As a dietary supplement, Mo is usually in the form of sodium molybdenate or ammonium molybdenate and is a common ingredient in over-the-counter multivitamins (Hendler and Rorvik, 2008). Although Mo is added to a number of supplements, Mo nutritional requirements are met in a typical US diet.

2.3 Sources

Contributions to Mo soil concentrations can result from natural weathering processes and are dependent on the types of rock in the area; black shale and phosphorite have the highest concentrations of Mo on average and are associated with soil rich in Mo (US EPA, 1979, p. 31). Anthropogenic sources of Mo in soils include several industrial sources such as mining, milling, and smelting, as well as soils amended with fly ash, liquid sludge, or other Mo-enriched media for agricultural purposes (Eisler, 1989, p. 10).

Industries also contribute to elevated Mo in surface water bodies, streams, and groundwater. In particular, the mining, milling, and smelting of Mo can contaminate nearby water bodies. Other industries that may release excess amounts of Mo into the environment (and particularly water) include uranium and copper mining and milling, shale oil production, and coal-fired power generation (US EPA, 1979). Of these other sources, in particular, uranium extraction from ore is associated with Mo contamination. This is because these two compounds are often co-located (US EPA, 1979).

Lastly, additional sources contributing to elevated Mo concentrations include industrial uses in alloys, flame retardants, catalysts, lubricants, and corrosion inhibitors (Barceloux, 1999; Buekers *et al*., 2010). Also, biosolid application as fertilizer may increase Mo soil concentrations (O’Connor *et al*., 2001).

3

HUMAN HEALTH EFFECTS

This chapter focuses on the human health effects of Mo, including its essential and beneficial properties at lower doses and the adverse effects that can occur at higher exposures, beginning with a brief discussion of the human metabolism of Mo. This discussion includes information garnered from primary and secondary literature, and it is comprehensive with respect to human studies via oral exposure. Overall, human studies involving oral exposure are limited. Thus, to provide more insight into potential Mo toxicity, supplementary information on inhalation exposure and data from animal studies are also briefly reviewed. Additionally, this chapter describes how health-based information on Mo was used to develop toxicity criteria, cancer classifications, and other regulatory limits.

3.1 Uptake, Bioavailability Metabolism, and Excretion in the Human Body

When ingested, water-soluble forms of Mo are readily absorbed by the gastrointestinal tract, while poorly soluble compounds (*e.g.*, Mo disulfide) are minimally absorbed (Barceloux, 1999; Vyskocil and Viau, 1999). Overall, several key studies conducted in humans indicate that Mo absorption ranges from 28-95% following oral intake (Alexander *et al*., 1974; Robinson *et al*., 1973; Turnlund *et al*., 1995). In these studies, however, the chemical form of ingested Mo was not described, and therefore the solubility and bioavailability of Mo in these tests cannot be ascertained; this may account for the wide range of absorptions measured. Animal studies provide information on the forms of Mo that undergo the most significant absorption. Vyskocil and Viau (1999) report that absorption of various forms of Mo (from highest to lowest) is: $MoO_4^{2-} > MoO_3 > (NH_4)_2MoO_4 > MoS_2$ (V). Recent evidence suggests that food-bound Mo has lower bioavailability than purified Mo (Novotny and Turnlund, 2006).

Once absorbed, Mo distributes rapidly to the blood and most organs (Barceloux, 1999; Vyskocil and Viau, 1999). Blood Mo concentrations have been reported to be 5 μg/L on average, but levels as high as 400 μg/L have been measured after elevated exposures (Allaway *et al*., 1968). Upon exposure, the highest concentrations of Mo have been found in the kidney and liver, with lower levels in the adrenal glands and long bones (Barceloux, 1999; Vyskocil and Viau, 1999). Mo does not bioaccumulate in tissues and, after exposure cessation, tissue concentrations decrease to steady-state levels in a relatively short timeframe in most organs (Schroeder *et al*., 1970; Barceloux, 1999; Vyskocil and Viau, 1999). The biological half-time for Mo in humans has not been studied extensively. Limited studies suggest that half-times in animals vary from a few hours to several days (Vyskocil and Viau, 1999).

Mo is excreted primarily via the urine or feces (Barceloux, 1999; Vyskocil and Viau, 1999; Turnlund *et al*., 1995). Animal and human studies show similar excretion profiles and indicate that very little Mo is excreted via the bile (Vyskocil and Viau, 1999). In addition, Mo compounds have been found to readily cross the placental barrier (Bougle *et al*., 1989; Barceloux, 1999).

3.2 Measurement in Human Biological Media

The analysis of Mo concentrations in biological media is difficult because of background contamination issues (Barceloux, 1999). Urinary concentrations are the preferred measure of exposure because this is the primary excretion route of Mo, and urinary concentrations have been found to be highly correlated with dietary intake (IOM, 2001). The National Health and Nutrition Examination Survey (NHANES III) of US residents reported a 95th percentile concentration of 168 mg Mo/L in urine (Paschal *et al*., 1998; Barceloux, 1999). Although urinary measurements may be more reliable, a recent study has demonstrated that plasma Mo can reflect differential dietary intakes of Mo and may be a useful indicator of Mo exposure under certain conditions (Turnlund and Keyes, 2004).

3.3 Health Effects

Very little information exists on the health effects of Mo in humans, both beneficial and adverse (Barceloux, 1999). As described in more detail in the following sections, some of the more informative studies on potential adverse health effects come from studies in populations living in areas rich in Mo. Occupational studies also provide some information on health impacts from inhalation exposure. Much of the toxicology information available, however, is from animal studies.

3.3.1 Essentiality and Health Benefits

Mo is essential to normal biological function. Mo serves as a co-factor for several enzymes in humans and animals that are important for metabolism of sulfur amino acid and heterocyclic compounds (IOM, 2001). For example, Mo is a co-factor for sulfite oxidase, an enzyme that catalyzes the oxidation of sulfite to sulfate and is necessary for metabolism of sulfur amino acids (IOM, 2001; Turnlund *et al*., 1995). Sulfite oxidase deficiency or absence leads to neurological symptoms and early death (IOM, 2001; Turnlund *et al*., 1995). Also, Mo is necessary for xanthine oxidase activity, which is involved in xanthine metabolism and the normal production of uric acid (IOM, 2001; Turnlund *et al*., 1995). Low dietary Mo leads to low urinary and serum uric acid concentrations and excessive xanthine excretion (IOM, 2001; Turnlund *et al*., 1995). While these biochemical changes have not been reported to be associated with clinical signs of Mo deficiency in adults, metabolic defects of molybdoenzymes in infants have been reported to result in mortality or severe neurological abnormalities (IOM, 2001). Based on potential health concerns associated with Mo deficiency, the Institute of Medicine (IOM) of the National Academy of Sciences (NAS) has developed recommended dietary allowances (RDAs). These RDAs are presented in Table 3-1. Consistent with these RDAs, recent studies of Mo metabolism have demonstrated that an intake of 43 μg/day would be sufficient to maintain plasma Mo levels at the necessary steady state in healthy adults (Novotny and Turnlund, 2006; 2007).

Table 3-1
Recommended Dietary Allowances for Molybdenum

Life Stage Group	RDA (µg/day)[1]
Infants	
0-6 mo	2 (adequate intake)
7-12 mo	3 (adequate intake)
Children	
1-3 y	17
4-8 y	22
Males/Females	
9-13 y	34
14-18 y	43
19 to > 70 y	45
Pregnancy/Lactation	
≤18 y	50
19-30 y	50
31-50 y	50

Notes: [1] RDA = Recommended Dietary Allowance; the average daily dietary nutrient intake level sufficient to meet the nutrient requirement of nearly all healthy individuals in a particular life stage and gender group.

Source: IOM (2001).

3.3.2 Antagonistic Effects

Mo metabolism is affected by the presence of copper, sulfate, and tungsten (NTP, 1997). Mo salts can alter copper absorption by forming copper molybdate or thiomolybdate compounds, two compounds that are poorly absorbed (Vyskocil and Viau, 1999; NTP, 1997). Sulfate can alleviate Mo toxicity by reducing gastrointestinal absorption; however, in copper deficient states, sulfate can aggravate symptoms in mammals (Vyskocil and Viau, 1999; NTP, 1997). Copper, sulfate, and copper-sulfate have been used to treat health effects associated with excessive Mo intake (NTP, 1997). Conversely, ammonium tetrathiomolybdate has been used to alleviate chronic copper poisoning in ruminants, and it has been suggested as a possible treatment for Wilson's disease (Haywood *et al*., 1998; Brewer, 2003). Similarly, because copper has been suggested to play a role in Alzheimer's disease, animal studies have demonstrated that treatment with tetrathiomlybdate can reduce beta amyloid levels (a hallmark of Alzheimer's disease) and memory impairment (Quinn *et al*., 2010). Tungsten and Mo also act antagonistically and, as a result, tungsten can alter both the absorption and function of Mo (De Renzo, 1962; Cohen *et al*., 1973; NTP, 1997).

3.3.3 Acute Health Effects

Available information on the acute effects following high Mo exposures, particularly in humans, is limited. Momcilovic (1999) reported an incident of Mo poisoning from a nutritional supplement. A cumulative dose of 13.5 mg Mo (300-800 μg Mo/day[1]) was consumed over 18 days and resulted in a number of neurological effects that were persistent a year after exposure (Momcilovic, 1999). No information on lethal doses in humans is available. Lethal doses for animals range from 3-333 mg/kg-day, depending on the exposure period and animal species (Vyskocil and Viau, 1999).

3.3.4 Chronic Non-Cancer Health Effects

3.3.4.1 Oral Exposures

Four studies have evaluated the potential health effects from chronic Mo exposure in humans (Koval'skiy *et al.*, 1961; Deosthale and Gopalan, 1974; US EPA, 1979; Meeker *et al*, 2010). In a cross-sectional epidemiology study in Armenia, Koval'skiy *et al.* (1961) correlated the dietary intake of Mo with serum uric acid levels and several other biochemical endpoints with a gout-like sickness affecting the adult population in two settlements. This region had a naturally high Mo content in the soil and plants (38 and 190 times that of the control area) and a low content of copper. Dietary Mo intake was estimated at doses of 0.14-0.21 mg/kg-day for a 70-kg adult. Medical exams performed in highly exposed areas indicated that 57 adults (31% of the adult population) from one settlement and 14 adults (17.9% of the adult population) from the other had gout-like symptoms, compared with 1-4% on average for the area. This condition was characterized by pain, swelling, inflammation and deformities of the joints, and, in all cases, an increase in the uric acid content of the blood (Koval'skiy *et al.*, 1961). In a number of cases (exact number not reported), this condition was accompanied by illnesses of the gastrointestinal tract, liver, and kidneys (US EPA, 2003). Both serum Mo and serum xanthine oxidase activity were positively correlated with serum uric acid levels. Increasing urinary excretion of copper was inversely correlated to increasing serum levels of Mo.

Ingestion of Mo in drinking water was investigated in two Colorado cities over a two-year period (US EPA, 1979). Urinary levels of Mo and copper and serum levels of ceruloplasmin (the major copper-carrying protein in the blood) and uric acid were examined. The Mo intake was ≥ 7 μg/kg-day (≥ 0.0001 mg/kg-day) in the exposed group. Higher daily urinary Mo was associated with higher Mo intake; however, no adverse biochemical or systemic effects were noted (US EPA, 1979).

A recent cross-sectional epidemiology study explored the associations between exposure to metals and testosterone levels in 219 men recruited from infertility clinics (Meeker *et al.*, 2008, 2010). The authors reported a significant association ($p = 0.001$) between reduced testosterone levels and increased blood Mo levels (70th and 85th percentile blood Mo concentrations were 1.0 and 1.5 μg/L, respectively). The authors and reviewers of the study, however, noted several study limitations (*e.g.*, small sample size, uncertain blood Mo detection limits). Thus, further research is needed to confirm this association and its clinical relevance (Meeker *et al.*, 2008, 2010; Sorahan and Sullivan, 2009).

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[1] For a 70-kg adult, this translates to a dose of 0.004-0.01 mg/kg-day.

Lastly, in a controlled experiment, Deosthale and Gopalan (1974) examined the effects of dietary Mo exposure on uric acid and copper excretion in four adult men given diets based on sorghum varieties differing widely in Mo content for 10 days. The urinary excretion of uric acid was unaltered at Mo intake levels up to 1,540 µg/day (approximately 0.022 mg/kg-day), but copper excretion increased with increasing Mo dose (Deosthale and Gopalan, 1974; Vyskocil and Viau, 1999).

3.3.4.2 Inhalation Studies

In occupational settings, there have been reports that inhalation of Mo (*i.e.*, metallic Mo dusts or Mo-trioxide, MoO_3) may adversely affect health. Pneumoconiosis (restrictive lung disease) has been reported following inhalation exposure (Vyskocil and Viau, 1999). For example, in a study of 19 molybdenum wire workers exposed for four to five years to Mo in dust at concentrations ranging from 1-19 mg Mo/m^3, three workers showed signs of pneumoconiosis (Mogilevskaya, 1967; Vyskocil and Viau, 1999). In a plant producing Mo-trioxide, an eight-hour exposure to Mo-trioxide dusts was measured at 9.47 mg/m^3 (Walravens *et al.*, 1979). Mean serum uric acid levels of 25 male workers were significantly (1.18-fold) higher, and mean serum ceruloplasmin (copper transport protein) levels were also significantly (1.65-fold) higher than those of unexposed workers (Walravens *et al.*, 1979; NTP, 1997). In this study, the authors reported no evidence of a gout-like syndrome (Walravens *et al.*, 1979; NTP, 1997). Gout and multiple sclerosis, however, have been reported in several case studies of humans exposed to high Mo concentrations in air (Pitt, 1976; Walravens *et al.*, 1979; US EPA, 1975; Selden *et al*., 2005). For example, complaints of pain in joints (arthralgia) were reported in 37 copper-molybdenum plant workers with elevated serum uric acid levels (US EPA, 1975; NTP, 1997). Detailed methods and results are not available for these studies; thus, evaluating the validity of results is not possible (US EPA, 1975).

3.3.4.3 Animal Studies

Overviews of animal toxicity studies of Mo via oral exposure are available from several different sources (NTP, 1997; Vyskocil and Viau, 1999). Based on these publications, the health effects and associated levels of exposure are summarized in Table 3-2. Briefly, acute symptoms of Mo toxicity include diarrhea, coma, and death from cardiac failure (NTP, 1997). Sub-chronic or chronic exposures mainly lead to growth retardation, anemia, diarrhea, and changes to the thyroid, kidney, and liver (NTP, 1997; Vyskocil and Viau, 1999). Mo also was found to disturb bone metabolism, giving rise to lameness, bone joint abnormalities, osteoporosis, and high serum phosphatase levels (NTP, 1997; Vyskocil and Viau, 1999). Elevated Mo exposure also was found to adversely affect reproduction (*e.g.*, decreased gestation weight and offspring survival) (Vyskocil and Viau, 1999). The lowest observed adverse effect level (LOAEL) of Mo for the chronic symptoms described above range from 1.5-80 mg/kg-day and varied by animal species (Table 3-2).

Table 3-2
Lowest and No Observed Effect Concentrations from Animal Studies

Species	Effect	Exposure Duration (Form of Mo)	LOAEL (mg/kg-day)[1]	NOAEL (mg/kg-day)[1]	Source
Rat	Prolonged estrus cycle, decreased gestation weight, effect on embryogenesis	9 weeks (Na_2MoO_4)	16	0.9	Fungwe *et al*., 1990
Rat	Growth depression	13 weeks ($NaMoO_4$)	2	-	Jeter and Davis, 1954
Rat	Bone deformities	6 weeks (Na_2MoO_4)	7.5	-	Miller *et al*. 1956
Rat	Growth depression	13 weeks ($NaMoO_4$)	8	2	Jeter and Davis, 1954
Rat	Infertility	13 weeks ($NaMoO_4$)	8	2	Jeter and Davis, 1954
Rat	Anemia	5 weeks (Na_2MoO_4)	50	-	Ostrom *et al*., 1961
Rat	Diarrhea	5-8 weeks (Na_2MoO_4)	50	-	Cox *et al*., 1960
Rat	Renal failure	8 weeks ($[NH_4]_6\ Mo_70_{24}$)	80	40	Bompart *et al*., 1990
Rat	Male reproductive toxicity	2 months (tetrathiomolybdate-TTM)	12 (TTM) 4.4 (Mo)	4 (TTM) 1.5 (Mo)	Lyubimov *et al*., 2004
Rabbit	Reduced growth and histological changes in kidney and liver	6 months (MoO_2SO_4)	5	0.5	Asmanagulyan, 1965
Rabbit	Reduced growth, skeletal abnormalities, anemia	4 months (Na_2MoO_4)	23	46	Arrington and Davis, 1953
Rabbit	Skeletal abnormalities, anemia	5 weeks (Na_2MoO_4)	25	-	McCarter *et al*., 1962
Rabbit	Thyroidal injury	1 month (Na_2MoO_4)	66	-	Widjajakusuma *et al*., 1973
Rabbit	Testes histology and clinical chemistry	14 days ($[NH_4]_6\ Mo_70_{24}$)	1.2	-	Bersenyi *et al*., 2008
Guinea pig	Reduced growth	8 weeks (Na_2MoO_4)	75	-	Arthur, 1965
Mouse	Failure to breed, deaths of offspring and litters	3 generations (Molybdate salt)	1.5	-	Schroeder and Mitchener, 1971

Notes: *[1] NOAEL and LOAEL doses are based on molybdenum ion.*
LOAEL = lowest observed adverse effect level; NOAEL = no observed adverse effect level.
Adapted from Vyskocil and Viau (1999).

3.3.5 Cancer Health Effects

Information available to assess the carcinogenicity of Mo compounds is inconclusive (US EPA, 2003). Only a few human and animal studies have evaluated an association between Mo exposure and cancer incidence, and those have reported mixed results. Furthermore, data suggest that Mo deficiency may be associated with an increase in cancer incidence. A summary of cancer studies is provided below.

3.3.5.1 Human Studies

Studies regarding the carcinogenicity of Mo compounds in humans are limited, and these studies suffer from poor experimental designs and conflicting results (NTP, 1997). Robinson and Clifford (1968) found no correlation between an above-normal incidence of nasopharyngeal carcinoma and the concentrations of Mo in food crops and soil in the high-altitude areas of Kenya. In a case-control study, the relationship between lung cancer and Mo occupational exposure was investigated by questionnaires administered to male lung cancer patients (Droste *et al.*, 1999). The authors reported an association between occupational exposure (primarily inhalation) to Mo and lung cancer (Droste *et al.*, 1999). The authors commented that their study was the first to report a significant association, but they also noted methodological problems (*e.g.*, measures of exposure, job descriptions, and self assessments) that limited the reliability of the results. In contrast, low intake (deficiency) of Mo has been attributed to high incidences of esophageal cancer in South Africa among the Bantu of Transkei (Burrell *et al.*, 1966) and in China (Luo *et al.*, 1983) and Russia (Nemenko *et al.*, 1976, as cited in NTP, 1997).

3.3.5.2 Animal Studies

Carcinogenicity studies in animals are also limited. No long-term bioassays to test Mo carcinogenicity via the oral route were identified. Two-year inhalation studies (6 hours/day, 5 days/week, 105 weeks) were conducted with rats and mice exposed to 0, 10, 30, or 100 mg/m^3 Mo-trioxide (NTP, 1997). Based on these studies, the National Toxicology Program (NTP) concluded that the evidence in rats was equivocal or negative, while in mice there was “some evidence of carcinogenicity…based on increased incidences of alveolar/bronchiolar adenoma and adenoma or carcinoma” (NTP, 1997).

Mo (III) trioxide was also found to be weakly carcinogenic in a short-term lung adenoma assay with mice (Stoner *et al.*, 1976). In this study, three groups of 20 mice were intraperitoneally injected with 50, 144, or 250 mg Mo (III) trioxide per kg body weight in normal saline three times per week for a total of 19 injections. The total doses received by each group were 950, 2,735, and 4,750 mg/kg. After 30 weeks, the frequency of lung tumors in the 4,750 mg/kg group was significantly higher than that in the controls, while tumor incidences in the two lower dose groups were similar to the controls (Stoner *et al.*, 1976).

Conversely, sodium molybdate was reported to reduce the incidence of tumors in rodents induced by nitroso compounds (NTP, 1997). Genotoxicity assays with bacterial strains and chromosomal aberration studies with Chinese hamster ovary cells generally have been negative for Mo compounds (NTP, 1997).

Overall, there is no evidence that Mo is carcinogenic via the oral route of exposure and, while there is some evidence of carcinogenicity in animals via inhalation, the human evidence is weak.

US EPA has concluded that the carcinogenicity of Mo has not been evaluated adequately in humans or animals (US EPA, 2003) and, therefore, it has not made a determination as to the carcinogenic potential of Mo.

3.4 Human Health Risk Assessment

Non-cancer and cancer toxicity information is used to develop chemical-specific toxicity factors that are used to quantitatively evaluate human health risks. Reference doses (RfDs) are used to assess non-cancer risks, and cancer slope factors (CSFs) are generally used to evaluate cancer risks. All US EPA-derived toxicity factors are published on the Integrated Risk Information System (IRIS). The IRIS database serves as an important resource because it allows scientists to standardize the risk assessment process by using a common set of toxicity criteria.

3.4.1 Evaluation of Non-Cancer Risks

As defined by US EPA, an RfD is intended to represent a level of daily human exposure, experienced over the course of a lifetime, that is likely to be without an appreciable risk of deleterious effects, even for susceptible members of the population (US EPA, 1993). For non-cancer risks, a threshold for chemical toxicity is typically assumed (*i.e.*, there is a dose below which adverse health effects are not observed). To derive an RfD, the chemical-specific threshold dose must be defined. This is accomplished by identification of a LOAEL and/or a no observed adverse effect level (NOAEL), from either human epidemiology or laboratory animal toxicology studies. After determining the NOAEL or LOAEL, this dose is divided by uncertainty factors (UFs) to account for potential uncertainties (including inter- and intra-species differences in sensitivity, insufficient study durations, use of a LOAEL instead of a NOAEL, and data deficiencies) to arrive at a final RfD. The application of UFs in the derivation of the RfD helps ensure that the RfD is health-protective. It should be noted that, according to US EPA, “it should not be categorically concluded that all doses below the RfD are ‘acceptable’ (or will be risk-free) and that all doses in excess of the RfD are ‘unacceptable’ (or will result in adverse effects)” (US EPA, 1993).

3.4.2 Derivation of the US EPA Oral Reference Dose

US EPA (2003) derived an oral RfD for Mo in 1993 based on the results of a six-year to lifetime dietary exposure study (Koval’skiy *et al.*, 1961). This study, which was described in more detail in Section 3.3.4.1, demonstrated that dietary intake of Mo was correlated with serum uric acid levels, several biochemical endpoints, and a gout-like sickness in an adult population in two Armenian settlements. Estimates of daily intake in the Mo-rich area for an average adult were 10-15 mg, corresponding to doses of 0.14-0.21 mg/kg-day for a 70-kg adult. In comparison, the control-area adults ingested 1-2 mg of Mo daily (0.014-0.029 mg/kg-day). Further analysis was conducted to correlate uric acid levels to Mo intake. It was estimated that a Mo intake of 0.14 mg/kg-day may result in serum uric acid levels above the range typically measured in adult populations (US EPA, 2003).

The Mo intake of 0.14 mg/kg-day was selected by US EPA (2003) as the critical value (*i.e.*, LOAEL) for use in developing an RfD. A final RfD of 0.005 mg/kg-day was derived by applying

UFs to the LOAEL. A UF of 3 was applied to protect sensitive human populations,[2] and a factor of 10 was applied for the use of a LOAEL, rather than a NOAEL, from a long-term study in a human population. US EPA (2003) indicated that the level of confidence in the oral RfD for Mo is "medium." According to IRIS, this confidence rating was based on the use of a study from a relatively large population and the fact that the proposed RfD satisfies Mo nutrient requirements for all healthy members of the population (US EPA, 2003).

3.4.3 Derivation of the Tolerable Upper Intake Levels

Although not used as commonly in risk assessment, IOM (2001) has recently developed a Tolerable Upper Intake Level (TUL) for Mo (Table 3-3). Under the IOM definition, the TUL is the highest level of a daily nutrient intake that is likely to pose no risk of adverse health effects for almost all individuals. IOM (2001) examined the available data and identified a NOAEL of 0.9 mg/kg-day[3] for Mo based on reproductive effects identified in rats and mice reported by Fungwe *et al*. (1990). This value was divided by a UF of 30 to obtain a safe dose level of 0.03 mg/kg-day for humans. Lastly, TULs were estimated for the various age groups by multiplying the safe dose of 0.03 mg/kg-day by average body weights, as shown in Table 3-3 (IOM, 2001). For example, 0.03 mg/kg-day multiplied by 68.5 kg (average adult male body weight) resulted in a TUL of 2,000 µg/day (rounded).

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[2] US EPA determined a full UF of 10 was not necessary for the protection of sensitive human populations because the study was conducted in a relatively large human population (US EPA, 2003).

[3] The US EPA RfD and IOM TUL are different due to the selection of different critical studies for developing the threshold level. The US EPA RfD is based on a study in humans, while the IUM TUL is based on an animal study. In addition, the RfD and TUL values were developed using differing UFs and assumptions.

Table 3-3
Tolerable Upper Intake Levels Established by the IOM

Life Stage Group	TUL (µg/day)
Infants	
0-6 mo	not established
7-12 mo	
Children	
1-3 y	300
4-8 y	600
Males/Females	
9-13 y	1,100
14-18 y	1,700
19 to > 70 y	2,000
Pregnancy/Lactation	
≤18 y	1,700
19-30 y	2,000
31-50 y	2,000

3.4.4 Evaluation of Cancer Risks

As discussed above, studies on the cancer effects associated with Mo exposure are limited and US EPA has concluded that this information is not adequate to evaluate Mo's carcinogenic potential in humans or animals (US EPA, 2003). Therefore, US EPA (2003) has not derived a CSF for Mo. In addition, Mo has not been evaluated formally by the International Agency for Research on Cancer (IARC) for its carcinogenic potential.

3.4.5 Regulations and Screening Criteria in Tap Water and Soils

Regulatory standards and criteria for environmental media are derived using toxicity criteria (RfDs and CSFs), human exposure assumptions, and other information. For drinking water, US EPA establishes Maximum Contaminant Level Goals (MCLGs) and Maximum Contaminant Levels (MCLs). An MCLG is a non-enforceable regulatory standard that, according to US EPA, reflects "the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety" (US EPA, 2009b). An MCL is set as close to the MCLG as possible while considering factors such as feasibility and cost benefit. US EPA has not established an MCLG or MCL for Mo; however, a health advisory and drinking water equivalent level (DWEL) has been published by US EPA (2009b) (See Table 3-4). A health advisory is an "estimate of acceptable drinking water levels for a chemical substance based on health effects information" and "is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, State, and local officials." A DWEL is "lifetime exposure concentration protective of adverse, non-cancer health effects, which assumes that all of the exposure to a contaminant is from drinking water" and is not an enforceable standard (US EPA, 2009b).

US EPA Regions III, VI, and IX have harmonized risk-based screening levels for use at Superfund Sites (US EPA, 2010b). These screening criteria are called regional screening levels (RSLs). RSLs are risk-based concentrations derived from standardized equations combining exposure information assumptions with US EPA toxicity data. RSLs are considered by US EPA to be protective for humans (including sensitive groups) over a lifetime. The RSLs are used for site "screening" and as initial cleanup goals, if applicable (US EPA, 2010b). RSLs are not *de facto* cleanup standards and should not be applied as such (US EPA, 2010b). The role of the RSL in site "screening" is to help identify areas, contaminants, and conditions that require further federal attention at a particular site. Chemical concentrations above the RSL would not automatically designate a site as "dirty" or trigger a response action; however, exceeding an RSL suggests that further evaluation of the potential risks by site contaminants is appropriate (US EPA, 2010b). RSLs for Mo in tap water and soils are presented in Table 3-4.

In addition to US EPA assessments, WHO has established a guideline for Mo in drinking water. As shown in Table 3-4, the WHO guideline is 0.07 mg/L. This value was derived based on epidemiological studies conducted in Colorado (see Section 3.3.4.1) (WHO, 2003).

Table 3-4
Regulatory Screening Criteria for Molybdenum in Soil, Water, and Air

Source	Media	Criteria Concentration
US EPA Health Advisory[1]	Drinking Water	0.08 mg/L
US EPA DWEL[2]	Drinking Water	0.2 mg/L
WHO Drinking Water Guideline	Drinking Water	0.07 mg/L
US EPA RSL[3]	Tap Water Residential Soil Industrial Soil Soil Screening Value Protective of Groundwater	0.18 mg/L 390 mg/kg 5,100 mg/kg 3.7 mg/kg

Notes: [1] Health advisory for 1- or 10-day exposure for a 10-kg child.

[2] DWEL = drinking water equivalent level; DWEL is estimated using the RfD (0.005 mg/kg-day) and assumes a 2 Liter/day drinking water intake and a 70 kg body weight.

[3] RSL = regional screening level.

3.5 Risk Assessment of Molybdenum in Coal Combustion Products

A recent draft US EPA risk assessment found that CCPs stored in unlined landfills pose a potential Mo health risk (US EPA, 2010a). US EPA estimated that Mo leaching of coal combustion waste (CCW) from unlined waste management units to groundwater could reach levels that, if consumed by humans, would exceed the RfD by 8-fold (US EPA, 2010a). This exceedance was for a maximally exposed individual (90th percentile) only; the RfD was not exceeded for an individual when modeling a more typical exposure scenario. It should be noted that the calculated risk exceedance reflects several health protective assumptions with regard to the leaching model, exposure assumptions, and toxicity criteria. The fate and transport of Mo and leaching behavior are discussed in more detail in Chapters 5 and 6.

An earlier risk assessment conducted by US EPA on the storage of CCPs focusing on non-groundwater pathways (*i.e.*, residential exposures from soil ingestion, inhalation, gardening, beef and dairy consumption, and erosion and overland transport) did not identify an Mo-related risks (US EPA, 1998).

3.6 Human Health Risk Assessment Toolbox

Government websites and reports provide useful information on risk assessment. The list below presents some of the key human health risk assessment resources. Some resources are specific to Mo, while others present information on a wider range of environmental contaminants.

3.6.1 Molybdenum-Specific Resources

- US EPA's IRIS file for Mo (CASRN 7439-98-7) (US EPA, 2003) Website: http://www.epa.gov/iris/subst/0425.htm
- International Molybdenum Association's (IMOA) Database of Molybdenum in Human Health and the Environment Website: http://www.imoa.info/HSE/environmental_data/database.html
- Molybdenum in Drinking-water: Background Document for Development of WHO Guidelines for Drinking-water Quality http://www.who.int/water_sanitation_health/dwq/chemicals/molybdenum.pdf

3.6.2 General Resources

- US EPA's RSL Summary Table: http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/Generic_Tables/pdf/master_sl_table_run_MAY2010.pdf

4
ECOLOGICAL EFFECTS

As discussed in Chapter 3, Mo is an essential nutrient for microorganisms, plants, and animals, but adverse effects can result from exposures in excess of nutritional requirements. Both natural and anthropogenic sources can result in elevated levels of Mo in soil and water, two of the critical exposure routes for ecological receptors (*e.g.*, plants and animals). In this chapter, Mo bioavailability, uptake, bioaccumulation, and toxicity in aquatic and terrestrial organisms are summarized. In addition, available ecological screening benchmarks (*i.e.*, threshold concentrations above which adverse ecological effects might occur) and regulatory guidelines for protection of ecological receptors are presented.

Extensive reviews of Mo ecotoxicity were performed by the US Fish and Wildlife Service (US FWS) in 1989, US Department of the Interior (US DOI) in 1998, and the Dutch National Institute for Public Health and the Environment (RIVM) in 1992 and 2005 (Eisler, 1989; US DOI, 1998; van de Plassche *et al*., 1992; RIVM, 2005). These Mo ecotoxicity data compilations and reviews are the primary sources of data reviewed here. US EPA’s Ecotoxicological (ECOTOX) Database was also queried (November 2010) and all data not overlapping in Eisler (1989), US DOI (1998), and/or RIVM documents (van de Plassche *et al*., 1992; RIVM, 2005) were also evaluated. In addition, recent publications on Mo ecotoxicity were searched on several sources (*e.g.*, PubMed, WorldCat, Scopus, and Google). All relevant publications were identified and included for review. Data presented here should be considered comprehensive but not exhaustive.

4.1 Bioavailability, Uptake, and Bioaccumulation in Ecological Receptors

4.1.1 Factors Affecting Molybdenum Bioavailability in Ecological Receptors

Molybdate is the predominant water-soluble Mo species under environmental conditions. Molybdate is also the Mo species that plants and animals take up most readily from soil and water. Several different environmental factors influence the extent of Mo uptake, bioaccumulation, and toxicity. For example, differences in soil pH, soil organic carbon (OC), aluminum and iron oxide, and soil sulfate (SO_4^{2-}) were examined across 10 soils (van Gestel *et al*., 2010). These factors influenced Mo toxicity in soil invertebrates (*e.g.*, earthworms, collembola, and enchytraeids), with toxicity varying between 18- to > 47-fold across the 10 soils (van Gestel *et al*., 2010). Similarly, Mo toxicity in higher plants (*e.g.*, oilseed rape, red clover, ryegrass, and tomato) varied between 66- to 609-fold across the 10 different soils (McGrath *et al*., 2010a,b).

By sequestering Mo, soil iron and aluminum oxides reduce the molybdate concentration in soil pore water, especially in acidic soils, thus limiting Mo uptake in plants and other soil organisms (Bibak and Borggaard, 1994; US EPA, 1998, Appendix I; McGrath *et al*., 2010b; van Gestel *et al*., 2010). Similarly, increased soil OC decreases Mo toxicity. Mo sequestration by iron oxides bound to soil OC and/or direct Mo sequestration by soil OC are believed to reduce the amount of Mo available for uptake (McGrath *et al*., 2010b). Direct Mo adsorption to soil humic acid (a major fraction of soil OC) also has been demonstrated to reduce uptake and, ultimately, toxicity (Bibak and Borggaard, 1994).

Molybdate and sulfate have similar structures and environmental behavior (Zimmer and Mendel, 1999; McGrath *et al*., 2010b; van Gestel *et al*., 2010). This explains why sulfate in soil competes with Mo uptake by some plants and can modulate Mo toxicity. In Mo-deprived soils, specific Mo transporters maintain essential Mo status in plants, but in Mo-rich soils much of the Mo is taken up via the sulfate transporters (McGrath *et al*., 2010b).

The presence of other metals (*e.g.*, copper) and anions (*e.g.*, phosphate) also can affect Mo bioavailability and toxicity in the environment. Interactions between copper, Mo, and sulfur are known to alter Mo effects in ruminants (*e.g.*, livestock) (Suttle, 1991; O'Connor *et al*., 2001; Helz and Erickson, 2011). For example, studies indicate ruminants feeding on diets low in Mo and sulfur and moderate in copper content can succumb to copper toxicity; conversely, diets high in Mo and sulfur and moderate in copper content can result in copper deficiency (Suttle, 1991; O'Connor *et al*., 2001). Phosphate also competes with molybdate to bind to aluminum oxide (Goldberg, 2010); therefore, its presence in environmental media may increase Mo bioavailability.

Studies on the environmental factors affecting Mo interactions are focused largely on soils. The environmental factors that affect Mo uptake and/or toxicity, however, are likely to be operational in other environmental media (*e.g.*, in water and sediment) because similar interactions among the substrates can also take place in these media.

4.1.2 Bioaccumulation in Ecological Receptors

Mo uptake by various forage plants (including grains and cereals) has been reviewed by O'Connor *et al*. (2001) in the context of assessing risks toward mammals grazing on pasture receiving biosolids. In this review, O'Connor *et al*. (2001) reported plant uptake factors ranging from < 0.1 (in non-legume forage) to 4.3 (in legumes in alkaline soils). Unlike plants, wildlife species do not appear to accumulate high levels of Mo. Mo levels were low (0.1-4.0 mg/kg dry wt) in livers and kidneys of nine wildlife species – including deer, squirrel, chipmunk, badger, beaver, marmot, and pika – collected from areas of high environmental Mo, with no evidence of adverse effects (Kienholz, 1977, as cited in Eisler, 1989).

Available bioconcentration data for aquatic species indicate that bioconcentration factors (BCFs) for algae and plants are generally higher than those for invertebrates and fish (Table 4-1). Mo bioconcentration by freshwater algae can result in residues up to 20 mg/kg without apparent damage (Sagaguchi *et al*., 1981, as cited in Eisler, 1989). BCFs of up to 25 have been reported for marine plankton (Goyer, 1986, as cited in Eisler, 1989), with much higher BCFs (up to 3,570) reported for periphyton[4] (Table 4-1).

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[4] Periphyton is a complex matrix of algae and heterotrophic microbes attached to submerged substrata in almost all aquatic ecosystems (http://www.epa.gov/bioiweb1/html/periphyton.html).

Table 4-1
Molybdenum Bioconcentration in Aquatic Organisms

Species	Test Concentration (µg/L)	Exposure Duration	BCF[1]	Reference
Aquatic Plants				
Blue-green alga (*Anabaena oscillaroides*)	0.005	1h	3,300	Ter Steeg *et al*. (1986) as cited in Eisler (1989)
	0.073	1h	550	
	25	1h	7-24	
Green alga (*Chlorella vulgaris*)	10,000	1h	490	Sakaguchi *et al*. (1981) as cited in Eisler (1989)
		20h	2,000	
Freshwater alga (*Nitella flexilis*)	0.014	25d	628	Short *et al*. (1971) as cited in Eisler (1989)
	3,300	24d	39	
Bryophyte (*Hygrohypnum ochraceum*)	30.3	10d	370	Carter and Porter (1997) from US EPA, 2007
Lake periphyton	0.014	24d	3,570	Short *et al*. (1971) as cited in Eisler (1989)
Aquatic Invertebrates				
Amphipod (*Gammarus sp*.)	3,300	24d	4.8	Short *et al*. (1971) as cited in Eisler (1989)
Clam (*Margaretifera margaretifera*)		15-24d	0.3-1.8[2]	
Crayfish (*Pacifiastacus leniusculus*)		24d	5.7-9.8[3]	
Fish				
Steelhead trout (*Oncorhynchus mykiss*)	0.014	Chronic	1,143[4]	Short *et al*. (1971) as cited in Eisler (1989)
	3,300	24d	0.6-5.4[5]	

Notes: *[1] Unless noted otherwise, the BCF values are based on whole body tissue residue.*
[2] Muscle/soft parts/shell.
[3] Muscle/carapace.
[4] Liver.
[5] Gastrointestinal-tract/gill/muscle/liver/spleen.

Aquatic animals showed large interspecies differences in their ability to accumulate Mo. Marine bivalve mollusks generally demonstrated 30-90 times (and up to 1,300 times) more Mo in their body than the ambient seawater (Eisler, 1981, as cited in Eisler, 1989). In contrast, other aquatic invertebrates shown in Table 4-1 have BCFs < 10. In fish collected from surface water (rainbow trout, *Oncorhynchus mykiss*), Mo concentrations in water only slightly affected tissue Mo accumulation; tissue residues ranged from 5-118 µg/kg wet wt in water with trace (< 6 µg/L) Mo concentrations, 10-146 µg/kg in water with low (6 µg/L) Mo concentrations, and 13-322 µg/kg in water with high (300 µg/L) Mo concentrations (Ward, 1973, cited in Eisler, 1989). A similar pattern was observed for kokanee salmon (*Oncorhynchus nerka*) collected from the same surface waters (Ward, 1973, cited in Eisler, 1989). Short *et al*. (1971, cited in Eisler, 1989; Table 4-1) have reported a BCF of 1,143 in the liver of steelhead trout chronically exposed to 0.014 μg/L Mo, but this observation appears to be atypical.

4.2 Essentiality and Health Benefits in Aquatic and Terrestrial Organisms

Mo is present in enzymes with essential biological functions involved in the biochemical cycle of nitrogen, sulfur, and phosphorus, including nitrate reduction, nitrogen fixation, and oxidase reactions (van Gestel *et al*., 2010). In plants, Mo's essential biochemical role in growth via its involvement in nitrogen fixation and nitrate reduction is well recognized (Schroeder *et al*., 1970, as cited in Eisler, 1989). For example, insufficient Mo retards nodulation and limits nitrogen fixation in legumes (IMOA, 2010b). Mo also is essential for growth in animals, as it influences purine oxidation, protein synthesis, phosphate ester hydrolysis, sulfide oxidation and sulfur metabolism, and iron transport and utilization (IMOA, 2010c). Additionally, metabolic relationships between Mo and other trace elements also may have beneficial effects. For example, in mammals, Mo can protect against poisoning by copper, mercury, chromium, and likely other trace elements (Eisler, 1989).

4.3 Aquatic Toxicity

The available data on the toxicity of Mo in aquatic organisms are presented in Tables 4-2, 4-3, and 4-4. Acute toxicity data were available for both freshwater and marine organisms; chronic toxicity data were available only for freshwater organisms.

As noted earlier, because of its environmental relevance, molybdate [either as sodium molybdate (Na-molybdate, Na_2MoO_4) or ammonium molybdate (NH_4-molybdate, $(NH_4)_6(Mo_7O_2)_4$) is the most commonly used form of Mo in ecotoxicity studies. Occasional studies have used Mo-trioxide, but, under environmentally relevant conditions, Mo-trioxide readily transforms into molybdate, causing slight acidification (*i.e.*, pH lowering) in the process. Consequently, the apparent differences in molybdate versus Mo-trioxide ecotoxicity are due not to the Mo valence state but rather to the pH effects (De Schamphelaere *et al*., 2010). Therefore, as a matter of simplification, the studies below describe Mo toxicity in general, with the assumption that observed toxicity occurred from the molybdate ion.

4.3.1 Acute Toxicity

Acute toxicity tests are conducted for short durations (compared to the test species' entire life span), and the toxicological endpoints are generally based on observed gross effects, such as mortality or immobilization. Table 4-2 presents acute toxicity information on Mo for several species of freshwater invertebrates (annelids, crustaceans, and insects) and fish species. The studies have been conducted at environmental pH of 6.7-8.5 and over a wide range of temperatures and water hardness levels. Reported endpoints are the 50% lethal concentration (LC50) and/or 50% effect concentration (EC50). Based on the reported endpoint values, acute toxicity of Mo to aquatic organisms varies by several orders of magnitude depending on organism species and environmental conditions. The LC50 values vary about 10-fold within fish species; as a group, however, they appear to be more tolerant to Mo toxicity than invertebrates. Upon further investigation, the remarkably low LC50 values (0.36-4.6 mg/L) for a midge

(*Chironomus plumsus*) and an annelid (*Tubifex tubifex*) reported by Fargasova (1997, 1998, and 1999, cited in RIVM, 2005) were determined to be unreliable in a regulatory evaluation by RIVM (2005). Based on the rest of the data in Table 4-2, the lethality of Mo ranges from 211 mg/L (*N. botia* 96h LC50) to > 2,000 mg/L (*O. nerka* 96h LC50); a single sub-lethal effect concentration of 29 mg/L (*T. tubifex* 96h EC50) also was reported.

Table 4-3 presents available data on acute toxicity of Mo for marine organisms. Several species of mollusks, crustaceans, and fish have been tested at various pH, salinity, and temperature conditions. Lethality to these marine species ranges from > 79.8 mg/L (*M. saxatilis* 96h LC50) to 2,600 mg/L (*C. variagtus* 96h LC50); sub-lethal effect concentrations range from 150 mg/L (*M. edulis* 96h EC50) to 1,900 mg/L (*C. virginica* 96h EC50). These acute toxicity values generally indicate that marine species are more tolerant to Mo exposures than freshwater species.

4.3.2 Chronic Toxicity

Chronic tests encompass a significant fraction of the test species' life span. The chronic endpoints are generally based on sub-lethal effects such as growth and reproduction. De Schamphelaere *et al*. (2010) compiled and critically reviewed the quality of available Mo chronic toxicity data on aquatic species and found that available data were inadequate to derive a no observed effect concentration (NOEC) for aquatic organisms in surface waters. Consequently, De Schamphelaere *et al*. (2010) conducted several supplementary chronic toxicity studies that provided more relevant data on chronic toxicity of Mo in fresh water organisms, including algae, higher plants, and amphibians. All available data on the chronic toxicity of Mo in freshwater organisms (sub-lethal effects only), regardless of their quality, are presented in Table 4-4. Generally, the reported endpoints are either NOECs or the 10% effects concentrations (EC10) for growth or reproduction. No chronic toxicity data for marine species were found.

A species sensitivity distribution based on EC10 values (Table 4-4) is depicted in Figure 4-1. Based on the EC10 values for Mo, species sensitivity are as follows: fish (*O. mykiss*, 36.9 mg/L) > water flea (*D. magna*, 62.8 mg/L) > algae (*P. subcapitata*, 74.3 mg/L) > frog (*X. laevis*, 115.9 mg/L) > midge (*C. riparius*, 121.4 mg/L) > rotifer (*B. calciflorus*, 193.6 mg/L) > snail (*L. stagnalis*, 211.3 mg/L) > duckweed (*L. minor*, 241.5 mg/L). The EC10 values vary among species by roughly 6-fold and vary within species by < 2-fold (*e.g.*, fish EC10 ranges from 36.9-90.9 mg/L; water flea EC10 ranges from 62.8-105.6 mg/L). While NOEC data are also available, an analysis comparing NOECs to establish sensitivity among species would be unreliable. This is because the NOECs may be driven largely by the test concentrations and, thus, may not give a completely accurate depiction of a "true" NOEC for a particular species.

Two studies using Mo-trioxide report NOEC/EC10 values that are generally lower than those using molybdate for the same species (HRC, 1996, and Kimball, 1978, cited in De Schamphelaere *et al*., 2010). As discussed previously, the apparently higher toxicity of Mo-trioxide compared to molybdate is likely due to pH effects. De Schamphelaere *et al*. (2010), however, deemed both of these studies to be unreliable.

Table 4-2
Acute Toxicity of Molybdenum to Freshwater Organisms

Species	Test Compound[1]	Test Conditions			Exposure Duration	Endpoint[2]	Value (mg/L)	Reference[3]
		pH	Temp (ºC)	Hardness (mg $CaCO_3$/L)				
Invertebrates								
Annelids								
Tubificid worm (*Tubifex tubifex*)	Na-molybdate	7.6	24.5	ND	96h	EC50	29	Khangarot (1991)
	NH_4-molybdate	7.8	20	311	96h	LC50	4.6[4]	Fargašová (1999)
Crustaceans								
Amphipod (*Crangonyx pseudogracilis*)	Na-molybdate	6.7-6.8	45-55	ND	96h	LC50	2,700	Martin and Holdich (1986)
Insects								
Midge (*Chironomus plumosus*)	NH_4-molybdate	7.7	20	ND	96h	LC50	0.36[4]	Fargašová (1997)
	NH_4-molybdate	7.8	20	80	96h	LC50	0.46[4]	Fargašová (1998)
Fish								
Sucker (*Catostomus latipinnis*)	Na-molybdate	7.9	25	144	96h	LC50	1940	Hamilton and Buhl (1997)
Mummichog (*Fundulus heteroclitus*)	Mo-trioxide	ND	20	7.9, 18.8	96h	LC50	230, 315[5]	Dorfman (1977)

Table 4-2
Acute Toxicity of Molybdenum to Freshwater Organisms (continued)

Species	Test Compound[1]	Test Conditions	Exposure Duration	Endpoint[2]	Value (mg/L)	Reference[3]	211	Pundir (1989)
Fish								
Rainbow trout (*Oncorhynchus mykiss*)	Na-molybdate	6.9-7.2	8, 12	14-32	96h	LC50	800, 1,320	McConnell (1977)
Sockeye salmon (*Oncorhynchus nerka*)	Na-molybdate	7.4-7.6	15-18	107	96h	LC50	> 2,000	Reid (2002)
Ticto barb (*Puntius ticto*)	NH_4-molybdate	8	16	53	96h	LC50	550	Pundir and Saxena (1990)

Notes: *ND = no data*

[1] Na-molybdate is sodium molybdate (Na_2MoO_4); NH_4-molybdate is ammonium molybdate [$(NH_4)_6(Mo_7O_2)_4$]; Mo-trioxide is molybdenum trioxide (MoO_3).

[2] EC50 = 50% effect concentration (effect was immobility); LC50 = 50% lethal concentration.

[3] All references were cited in RIVM (2005).

[4] Rejected for use in derivation of environmental risk limits (ERLs) by RIVM (2005).

[5] Author reports that pH (which was < 4 at test completion) was probable cause of mortality.

Table 4-3
Acute Toxicity of Molybdenum to Marine Organisms

Species	Test Compound[1]	Test Conditions: pH	Test Conditions: Temp (ºC)	Test Conditions: Salinity (‰)	Test Conditions: Exposure Duration	Endpoint[2]	Value (mg/L)	Reference[3]
Mollusks								
Blue mussel (*Mytilus edulis*)	NH_4-molybdate	8.4	26	ND	48h	EC50[4]	150	Morgan *et al*. (1986)
Eastern oyster (*Crassostrea virginica*)	Na-molybdate	ND	20	ND	96h	EC50[5]	1,900	Knothe *et al*. (1988)
Crustaceans								
Green crab (*Carcinus maenas*)	Na-molybdate	5	12-14	33.2	48h	LC50	1,018[6]	Abbott (1977)
Pink shrimp (*Penaeus duorarum*)	Na-molybdate	ND	25	ND	96h	LC50	1,900	Knothe *et al*. (1988)
Mysid shrimp (*Mysidopsis bahia*)	Na-molybdate	ND	27	ND	96h	LC50	1,100	Knothe *et al*. (1988)
Amphipod (*Allorchestes compressa*)	NH_4-molybdate	5.0-5.4	16	34.8	96h	LC50	247	Ahsannulah *et al*. (1982)
Fish								
Sheepshead minnow (*Cyprinodon variegatus*)	Na-molybdate	ND	ND	25	96h	LC50	2,600	Knothe *et al*. (1988)
Striped bass (*Morone saxatilis*)	Na-molybdate	8.27	20	21	96h	LC50	> 79.8[7]	Dwyer *et al*. (1992)

Notes: ND = no data

[1] Na-molybdate is sodium molybdate (Na_2MoO_4); NH_4-molybdate is ammonium molybdate [$(NH_4)_6(Mo_7O_2)_4$].

[2] EC50 = 50% effect concentration; LC50 = 50% lethal concentration.

[3] All references were cited in RIVM (2005).

[4] Reproduction effects.

[5] Growth effects.

[6] Test described very poorly; endpoint is reported as TLM (median tolerance limit).

[7] Exposure concentration = 80% of nominal concentration.

Table 4-4
Chronic Toxicity of Molybdenum to Freshwater Organisms

Species	Test Compound[1]	pH	Exposure Duration	Endpoint[2]	Effect	Value (mg/L)	Reference
Green Algae							
Scenedesmus sp.	NH_4-molybdate	ND	96h	NOEC	Growth	54	Bringmann and Kuhn (1959) as cited in RIVM (2005)
Scenedesmus subspicatus	NH_4-molybdate	ND	72h	NOEC	ND	25	HRC (1994a) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	ND	72h	NOEC	ND	12.5	HRC (1994b) as cited in De Schamphelaere *et al*. (2010)
	Mo-trioxide	ND	72h	NOEC	ND	≥100	HRC (1994c,d) as cited in De Schamphelaere *et al*. (2010)
Pseudokirchneriella subcapitata	Na-molybdate	ND	72h	NOEC	ND	4.6	HRC (1996) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	8.0-8.1	72h	EC10	Growth rate	74.3-164[3]	De Schamphelaere *et al*. (2010)
Plant							
Duckweed (*Lemna minor*)	Na-molybdate	ND	7d	NOEC EC10	Growth rate	24.7 241.5	De Schamphelaere *et al*. (2010)
Invertebrates							
Rotifer (*Brachionus calyciflorus*)	Na-molybdate	7.5	48h	NOEC EC10	Population growth rate	244 193.6	De Schamphelaere *et al*. (2010)
Water flea (*Daphnia magna*)	Na-molybdate	ND	21d	NOEC	Reproduction	136[4]	GEI (2009) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	ND	21d	NOEC	ND	50	Diamantino *et al*. (2000) as cited in De Schamphelaere *et al*. (2010)
	Mo-trioxide	ND	21d	NOEC EC10	ND	4.41 6.98	Kimball (1978) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	7.4-8.2	21d	NOEC EC10	Reproduction	49.9-112 62.8-105.6	De Schamphelaere *et al*. (2010)

Table 4-4
Chronic Toxicity of Molybdenum to Freshwater Organisms (continued)

Species	Test Compound[1]	pH	Exposure Duration	Endpoint[2]	Effect	Value (mg/L)	Reference
Invertebrates							
Water flea (*Ceriodaphnia dubia*)	Na-molybdate	ND	7d	EC20	Reproduction	77[4]	GEI (2009) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	ND	8d	IC12.5	Reproduction	34	Naddy *et al*. (1995)
		7.6-7.9	7d	NOEC EC10	Reproduction	97.3 78.2	De Schamphelaere *et al*. (2010)
Midge (*Chironomus riparius*)	Na-molybdate	6.9-7.1	14d	NOEC EC10	Growth	393 121.4	De Schamphelaere *et al*. (2010)
Pond snail (*Lymnaea stagnalis*)	Na-molybdate	7.8-8.2	28d	NOEC EC10	Growth rate	200 211.3	De Schamphelaere *et al*. (2010)
Fish							
Rainbow trout (*Oncorhynchus mykiss*)	Na-molybdate	ND	32d 18mo	NOEC	ND	200-750 > 18.5	Davies *et al*. (2005) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	7.4±0.1	78/84d	NOEC EC10	Biomass	48.9-<121.0 36.9-43.2	De Schamphelaere *et al*. (2010)
Fathead minnow (*Pimephales promelas*)	Na-molybdate	ND	28d	EC10	Growth	90.9[4]	GEI (2009) as cited in De Schamphelaere *et al*. (2010)
	Na-molybdate	7.5±0.05	34d	NOEC EC10	Biomass	27.7 39.3	De Schamphelaere *et al*. (2010)
Cutthroat trout (*Oncorhynchus clarki*)	Na-molybdate	ND	30d	NOEC	ND	> 87.8	Pickard *et al*. (1999) as cited in De Schamphelaere *et al*. (2010)
Coho salmon (*Oncorhynchus kisutch*)	Na-molybdate	ND	20wk	NOEC	ND	> 19.5	Ennevor (1993) as cited in De Schamphelaere *et al*. (2010)

Table 4-4
Chronic Toxicity of Molybdenum to Freshwater Organisms (continued)

Species	Test Compound[1]	pH	Exposure Duration	Endpoint[2]	Effect	Value (mg/L)	Reference
Amphibian							
African clawed frog (*Xenopus laevis*)	Na-molybdate	7.8	4d	NOEC EC10	Malformation	22.4 115.9	De Schamphelaere *et al*. (2010)

Notes: *ND = no data*

[1] Na-molybdate is sodium molybdate (Na_2MoO_4); NH_4-molybdate is ammonium molybdate [$(NH_4)_6(Mo_7O_2)_4$]; Mo-trioxide is molybdenum trioxide (MoO_3).

[2] NOEC = no observed (adverse) effect concentration; EC10 = 10% effect concentration.

[3] Geometric mean of four values.

[4] Geometric mean of two values.

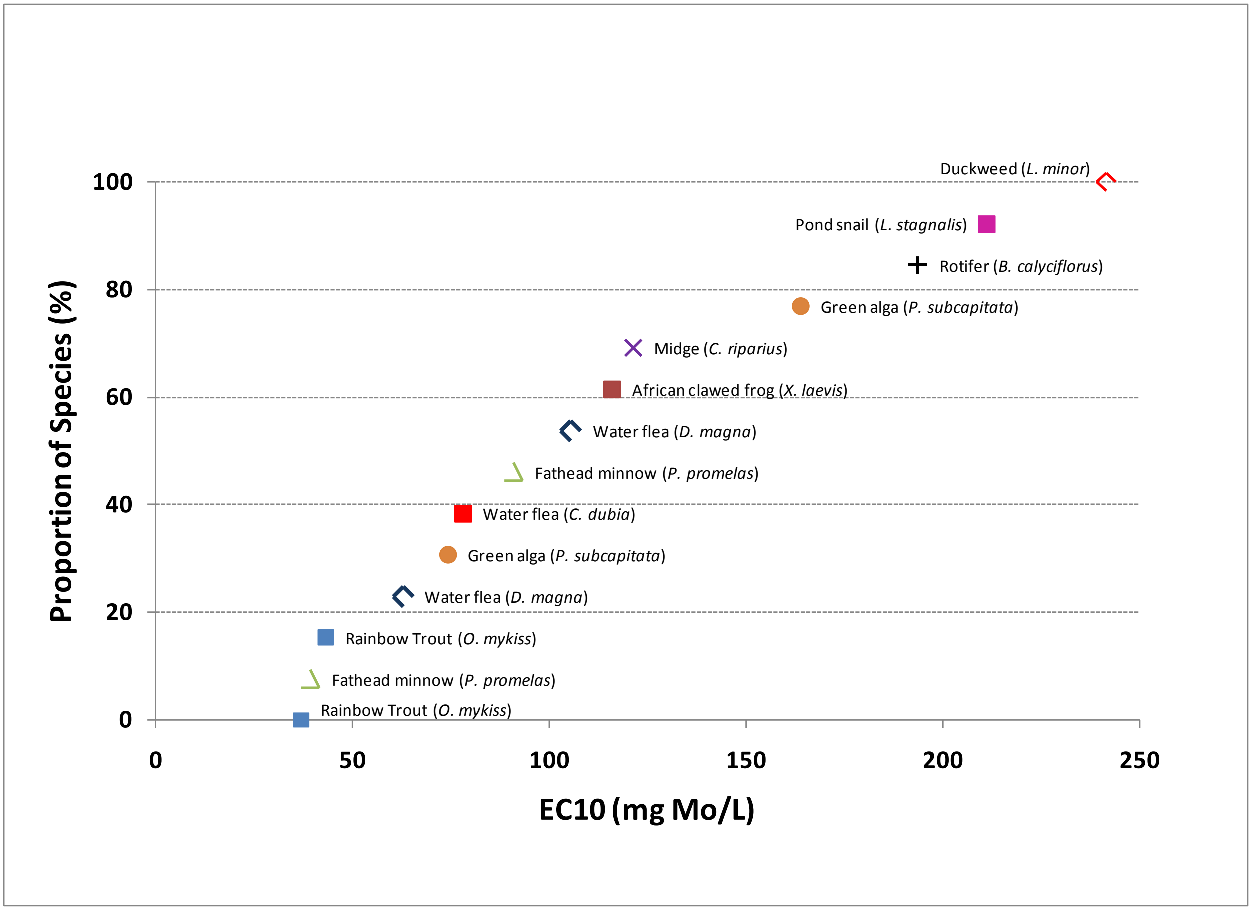


Figure 4-1
Species Sensitivity Distribution of Chronic Molybdenum Toxicity to Aquatic Organisms

Note: *Only EC10 values for molybdate from Table 4-4 are included; when a range of values was available, both the minimum and the maximum values are included.*

4.4 Terrestrial Toxicity

Most risk assessments for terrestrial organisms have focused on the likelihood of molybdenosis (a Mo-induced copper deficiency in ruminants) in cattle grazing on Mo-contaminated land (O'Connor *et al*., 2001). Effects on soil-dwelling organisms are relatively unexplored, and the limited data for microbial processes indicate that effects occur at high soil concentrations (> 480 mg/kg) that are not environmentally relevant (Buekers *et al*., 2010). Recently, Mo toxicity to invertebrates and plants has been investigated to support various regulatory risk assessments. A summary of these studies is presented in Table 4-5.

4.4.1 Effects on Soil Microbial Processes

Effects of Mo on several microbial processes and enzymatic activities have been tested in soils with wide-ranging properties [pH, soil organic matter (SOM), and clay contents]. The NOEC and EC10 values show a wide range (24-1,552 mg/kg dry wt soil) but generally exceed 120 mg/kg dry wt soil, indicating that soil microbes are generally tolerant of Mo exposure. However, it should be noted that, unlike aqueous solutions where experimental conditions can be controlled, transformation of test Mo compounds (Mo-trioxide, Na-,NH_4-,H_2-moblydate) in soils alters soil pH and salinity and, consequently, confounds effects attributable directly to Mo (Buekers *et al*., 2010). For example, as noted previously, the apparent effect of Mo-trioxide on highly pH-dependent nitrification (EC10 = 188 mg/kg in Table 4-5) was due entirely to changes in pH and salinity as Mo dose increased (Buekers *et al*., 2010). Therefore, after consideration of the confounding effects, Mo is expected to have relatively high toxicity thresholds for microorganisms.

4.4.2 Effects on Terrestrial Plants

As an essential trace element for the growth of all terrestrial plants, the presence of Mo in plants is not unexpected. In fact, all plants contain some Mo. The highest levels (> 20 mg/kg) are documented frequently in plants from contaminated areas. However, plants are generally tolerant of Mo and, in general, Mo accumulation in plants presents a greater concern to higher mammals exposed via their diet (such as mammals grazing on Mo-laden plants).

Buekers *et al*. (2010) studied the effects of Mo-trioxide and Na-molybdate on growth of wheat seedlings (*Triticum aestivum* L) in soil and determined EC10 values of 5 and 15 mg/kg, respectively (Table 4-5). However, after accounting for the confounding effects of pH and salinity, a lowest-effect concentration for Mo of 38 mg/kg was established for plants in soil. Based on these results, Buekers *et al*. (2010) recommended using Na-molybdate, with salinity controls, in soil toxicity studies. In another recent study, McGrath *et al*. (2010a) conducted plant growth studies using Na-molybdate in 10 soils with wide-ranging properties (Table 4-5). The EC50 values (not shown in Table 4-5) for a particular species varied by 66- to 609-fold across soils, whereas EC50s for a particular soil varied only 2- to 38-fold across the four species. The variability of toxicity thresholds across soils for a single species illustrates the importance of soil properties and their effects on Mo bioavailability (and ultimately toxicity). The toxicity threshold variability was less across different soils when they were based on soil solution Mo concentrations, highlighting that Mo bioavailability in soil depends on solubility. However, while using plant tissue as the metric produced a smaller range of EC50 values (compared to EC50 values derived using soil or soil solution concentrations), variability in Mo toxicity across soil types still persisted—indicating that Mo bioavailability is not explained by solubility alone. Effect concentration values quantified for Mo in plant shoots reflect a tolerance of plants to Mo uptake and accumulation. These studies showed that upwards of 200 mg Mo/kg plant tissue can accumulate without any adverse effects. Based on EC10 values, ryegrass was the most tolerant species.

Table 4-5
Molybdenum Toxicity to Soil Microbial Processes, Plants, and Invertebrates

Terrestrial Receptors	Soil Type/ Count	Test Compound [1]	Soil Properties			Test Conditions		Endpoint [3]	Effect	Value[4] (mg/kg dry wt)	Reference
			pH	SOM[2] (%)	Clay (%)	Temp (ºC)	Duration				
Microbial processes											
Nitrogen-mineralization	loam	H-molybdate	5.8	4.4	23	30	20d	EC10	Inhibition	480	Liang and Tabatabai (1977) as cited in RIVM (2005)
Nitrification	haplic luvisol	Mo-trioxide	5.0-6.4	ND	ND	ND	4d	EC10	Inhibition	188[5]	Buekers *et al.* (2010)
	haplic luvisol	Na-molybdate	6.2-6.6	ND	ND	ND	4d	EC10	Inhibition	1,552	
Alkaline phosphatase	silty clay loam	H-molybdate	7.4	9.3	34	37	0.5h	NOEC	Inhibition	120	Juma and Tabatabai (1977) as cited in RIVM (2005)
Arylsulfatase		H-molybdate	7	9	34	37	1h	NOEC	Inhibition	1,199	Al-Khafaji and Tabatabai (1979) as cited in RIVM (2005)
Urease	six soils	H-molybdate	5.1-7.8	2.6-9.3	17-42	37	0.5h	EC10	Inhibition	24-480	Tabatabai (1977) as cited in RIVM (2005)

Table 4-5
Molybdenum Toxicity to Soil Microbial Processes, Plants, and Invertebrates (continued)

Terrestrial Receptors	Soil Type/ Count	Test Compound [1]	Soil Properties			Test Conditions		Endpoint [3]	Effect	Value[4] (mg/kg dry wt)	Reference
Plants											
Wheat (*Triticum aestivum* L.)	haplic luvisol	Mo-trioxide/Na-molybdate	5.0-6.6	ND	ND	ND	21d	EC10	Growth (yield)	5-15[8]	Buekers *et al*. (2010)
Oilseed rape (*Brassica napus* L.)	10 field soils from Europe	Na-molybdate	4.4-7.8	0.6-30.7[9]	2-33	16-20	21d	ED10	Growth (shoot yield)	4-2,844	McGrath *et al*. (2010a)
Red clover (*Trifolium pratense* L.)										0.4-1,502	
Ryegrass (*Lolium perenne* L.)										14-3,476	
Tomato (*Lycopersicon esculentum* L.)										3-1,575	
Oilseed rape (*Brassica napus* L.)								EC10		2-140[6]	
Red clover (*Trifolium pratense* L.)										0.04-30[6]	
Ryegrass (*Lolium perenne* L.)										2-241[6]	
Tomato (*Lycopersicon esculentum* L.)										1.3-31[6]	
Oilseed rape (*Brassica napus* L.)								EC10		703 (185-1,220)[7]	
Red clover (*Trifolium pratense* L.)										225 (89-362)[7]	
Ryegrass (*Lolium perenne* L.)										228 (44-413)[7]	

Table 4-5
Molybdenum Toxicity to Soil Microbial Processes, Plants, and Invertebrates (continued)

Terrestrial Receptors	Soil Type/ Count	Test Compound [1]	Soil Properties			Test Conditions		Endpoint [3]	Effect	Value[4] (mg/kg dry wt)	Reference
Plants											
Tomato (*Lycopersicon esculentum* L.)										232 (63-402)[7]	
Invertebrates											
Earthworm (*Esenia andrei*)	10 field soils from Europe	Na-molybdate	4.4-7.8	0.6-30.7[9]	2-33	ND	4wk	NOEC	Repro-duction	8.88-≥2,744	van Gestel *et al*. (2010)
Enchytraeids (*Enchytraeus crypticus*)										78.1-≥2,820	
Collembola (*Folsomia candida*)										25.8-≥3,396	
Earthworm (*Esenia andrei*)								EC10		0.78-917	
Enchytraeids (*Enchytraeus crypticus*)										67.2-> 2,817	
Collembola (*Folsomia candida*)										38.9-> 3,396	

Notes: *ND = no data*

[1] Na-molybdate is sodium molybdate (Na_2MoO_4); H-molybdate is hydrogen molybdate (H_2MoO_4); Mo-trioxide is molybdenum trioxide (MoO_3).

[2] SOM = soil organic matter content.

[3] NOEC = no observed (adverse) effect concentration; EC10 = 10% effect concentration; ED10 = 10% effect dose.

[4] Unless noted otherwise, values are in terms of soil concentrations (in mg Mo/kg dry wt soil).

[5] Effects entirely due to changes in soil pH and not due to Mo.

[6] Values in terms of soil solution concentrations (in mg Mo/L soil solution).

[7] Values in terms of plant residue (in mg Mo/kg dry wt plant shoot), mean and range (all 10 soils).

[8] After correcting for the confounding effects, the EC10 is estimated to be 32 mg/kg.

[9] Organic carbon.

4.4.3 Effects on Terrestrial Invertebrates

Using the same 10 soils as the McGrath *et al*. (2010a) study, van Gestel *et al*. (2010) conducted studies of Mo toxicity on three species of soil invertebrates (earthworms, collembola, and enchytraeids). A summary of reported NOEC and EC10 values is shown in Table 4-5. Unlike for plants, toxicity thresholds varied more widely across species than across soil types, although Mo toxicity is dependent on both factors. The EC10 values for reproduction ranged from 0.78-917 mg/kg, 67.2 to > 2817 mg/kg, and 38.9 to > 3396 mg/kg for *E. andrei*, *E. crypticus*, and *F. candida*, respectively, indicating that *F. candida* was the most tolerant species, followed by *E. cryptis*; *E. andrei* was the most sensitive.

4.4.4 Effects on Terrestrial Vertebrates

We did not locate any studies on toxicity to birds in the environment. However, studies on domestic poultry exposed experimentally to a Mo-enriched diet were available. Based on these studies, birds appear to be tolerant to Mo. Adverse effects on growth were reported at dietary concentrations of 200-300 mg/kg, on reproduction at 500 mg/kg, and on survival at 6,000 mg/kg (Underwood, 1971, and Friberg *et al*., 1975, both as cited in Eisler, 1989). A few studies are available on the effects of Mo-related mining waste on animals (Kienholz, 1977, and King *et al*., 1984, both as cited in Eisler, 1989). Day-old chicks fed for 23 days with a diet containing 20% Mo mine tailings were unaffected; at 40% Mo mine tailings in diet, the chicks showed only a slight reduction in body weight (Kienholz, 1977, as cited in Eisler, 1989).

Studies on Mo ecotoxicity to mammalian wildlife are limited. Available studies focus mostly on domestic animals, such as livestock (cattle and sheep). Although direct effects of Mo on animal reproduction has been demonstrated (Phillippo *et al*., 1987, as cited in O’Connor *et al*., 2001), studies on livestock are almost always related to molybdenosis. Molybdenosis is characterized by Mo-induced copper deficiency (hypocuprosis) in ruminant animals, and was first identified in 1938 as the cause of severe diarrhea and emaciation in cattle grazing in areas called *teart* pastures (*e.g.*, pasture with alkaline pH and elevated Mo concentrations) in England (O’Connor *et al*., 2001). Ruminants are particularly sensitive to Mo, with adverse effects occurring at 2-20 mg/kg Mo in diet (when fed low copper diets) or when total daily Mo intake approaches 141 mg. The lethal dose to cattle is roughly 10 mg/kg body weight. Other mammals, including horses, pigs, rodents, and wildlife, are more tolerant to Mo. Mule deer (*Odocoileus hemionus*), for example, are at least 10 times more resistant than domestic ruminants; they can tolerate up to 1000 mg/kg, about the same as rabbits and rats (Ward and Naggy, 1977, and Anke *et al*., 1985, both as cited in O’Connor *et al*., 2001).

It is noteworthy that in the presence of excess sulfate, Mo may cause molybdenosis via copper-molybdenum-sulfate interactions, including formation of insoluble copper-molybdenum-sulfur complexes (*e.g.*, thiomolybdates). However, besides molybdenosis, there may be other causes of hypocuprosis. For example, as discussed in O’Connor *et al*. (2001), excess iron or sulfate may also exert an independent effect on copper availability, leading to hypocuprosis. Therefore, molybdenosis versus other causes of hypocuprosis needs to be evaluated carefully.

Overall, based on available data, birds (both wild and domestic) and mammalian wildlife are generally tolerant of elevated Mo exposures. Domestic mammals (cattle and sheep) appear to be the most sensitive. In 1980, the expert committee report of the NAS (the National Research

Council, or NRC) evaluated low-level, chronic Mo toxicity, and identified 5-10 mg/kg in soil as the critical level. This level is weakly associated with impaired bone development in young horses and cattle (NRC, 1980, as cited in O'Connor *et al*., 2001) and has been used in risk assessments of wild populations (O'Connor *et al*., 2001).

4.5 Ecological Risk Assessments

As noted in Chapter 2, mining activities, disposal of coal combustion residues (CCPs), and biosolids application constitute important anthropogenic sources of Mo in the environment. Although CCPs may be an anthropogenic source of Mo, recent US EPA risk assessments of CCPs have determined that Mo does not pose an ecological risk (US EPA, 1998, 2002, 2010a).

4.6 Ecological Regulatory Criteria and Screening Guidelines

Generally, the absence of regulatory criteria or guideline values for a substance may mean either that the substance is not a priority substance (*i.e.*, there is no potential environmental risk) or that there is a critical lack of data. For Mo, data on effects on mammalian species (domestic species) appear to be robust for deriving standards for protection from exposure via grazing (O'Connor *et al*., 2001), but data gaps have been identified for aquatic and other terrestrial species. Although some benchmarks based on the limited data do exist, new data using standard tests are being generated to support various risk assessments and the development of revised toxicity criteria for these ecological endpoints (De Schamphelaere *et al*., 2010; McGrath *et al*., 2010a; van Gestel *et al*., 2010). Available screening guideline values proposed for Mo by regulatory agencies and the scientific community are shown in Table 4-6 and discussed below.

Several surface water screening values for Mo are available from the National Oceanic and Atmospheric Administration's (NOAA's) Screening Quick Reference Tables (SQuiRTs) (Buchman, 2008) and RIVM (2005). The SQuiRTs were developed for screening purposes only and are very conservative (*i.e.*, over-protective). Environmental risk limits (ERLs) derived by RIVM serve as advisory values to set environmental quality standards (EQS) by the Dutch Ministry of Housing, Spatial Planning, and the Environment (VROM). The RIVM Maximum Permissible Concentration (MPC) is the concentration of a substance in a medium that should protect all species in ecosystems from adverse effects. The RIVM Ecological Serious Risk Concentration (SRC_{ECO}) is the concentration of a substance in a medium (soil, water, sediment, or air) at which an ecosystem's overall health will be seriously affected or is threatened. This is assumed when 50% of the species and/or 50% of the microbial and enzymatic processes could be affected. The Dutch Mo MPC of 30 µg/L for freshwater (Table 4-6) is very conservative, because it is based on a 100% protection (*i.e.*, no effects at all) whereas a protection for 95% of the species is typically considered in regulatory ecological risk assessments (ECB, 2003). To derive the Dutch freshwater MPC, a safety factor of 1,000 was applied to the EC50 (29 mg/L) for the annelid *T. tubifex* and added to the 90th percentile background surface water concentration in the Netherlands (1.3 µg/L).

Table 4-6
Regulatory and Scientific Molybdenum Screening Values and Standards for the Protection of Wildlife

Benchmarks	Symbol	Value	Units	Reference
Surface Water				
Dutch Guidance[1]				
Maximum Permissible Concentration	MPC	30	ug/L	RIVM (2005)
Ecological Serious Risk Concentration	SRC_{ECO}	54,000	ug/L	RIVM (2005)
NOAA SQuiRTs[2]				
Acute[a]		16,000	ug/L	Buchman (2008)
Chronic[b]		34	ug/L	Buchman (2008)
REACH Guidance Based[3]				
Median Hazard Concentration Affecting 5% of Species	HC_5	38,200	ug/L	De Schamphelaere *et al*. (2010)
Marine Water				
NOAA SQuiRTs[2]				
Chronic[b]		23	ug/L	Buchman (2008)
Groundwater				
NOAA SQuiRTs[2]				
Secondary Standards[c]		70	ug/L	Buchman (2008)
Dutch Standard[1]				
Target Value	TV_{GW}	5	ug/L	VROM (2009)
Soil				
NOAA SQuiRTs[2]				
Plants[d]	$Eco\text{-}SSL_{PLANTS}$	2	mg/kg	Buchman (2008)
Microbes[e]	$Eco\text{-}SSL_{MICROBES}$	200	mg/kg	Buchman (2008)
Dutch Guidance and Standards[1]				
Maximum Permissible Concentration	MPC	1.3	mg/kg	RIVM (2005)
Ecological Serious Risk Concentration	SRC_{ECO}	270	mg/kg	RIVM (2005)
Dutch Target Value[4]	TV_{Soil}	3	mg/kg	Buchman (2008)
Dutch Intervention Value[4]	IV_{Soil}	190	mg/kg	VROM (2009)

Benchmarks	Symbol	Value	Units	Reference
Biosolids Guidance[5]				
Ceiling Concentrations		75	mg/kg	O'Connor *et al*. (2001)
Cumulative Application Limit	RPc	40	kg/ha	O'Connor *et al*. (2001)
Alternate Pollutant Limit	APL	40	mg/kg	O'Connor *et al*. (2001)

Notes: *[1] Dutch Guidance and Standards:*

Maximum Permissible Concentration—Guidance concentration protective of all species in ecosystems from adverse effects.

Ecological Serious Risk Concentration—Guidance concentration that will seriously affect or threaten ecosystems (i.e., 50% of the species and/or 50% of the microbial and enzymatic processes are possibly affected).

Target Value (Standard)—Baseline concentration value below which compounds and/or elements are known or assumed not to affect the natural properties of the soil.

Intervention Value (Standard)—Maximum tolerable concentration above which remediation is required. This occurs if one or more compounds in concentrations equal to or higher than the intervention value are found in more than 25 m^3 *of soil or 1000 m*^{3} *of groundwater.*

[2] National Oceanic and Atmospheric Administration Screening Quick Reference Tables, which were developed for screening purposes only (Buchman, 2008).

[a] Based on Tier II Secondary Acute Value: http://www.esd.ornl.gov/programs/ecorisk/tools.html.

[b] Based on Australian and New Zealand ECLs and Trigger Values: ANZECC Oct 2000, Volume 1, The Guidelines: www.mfe.govt.nz/publications.

[c] Based on World Health Organization's (WHO's) drinking water guidelines: http://www.who.int/water_sanitation_health/dwq/en.

[d] Based on ORNL Screening Benchmarks (Efroymson et al., 1997a).

[e] Based on ORNL (Efroymson et al.,1997b).

[3] Predicted No Environmental Effect Concentration (PNEC) determined in accordance with the REACH Technical Guidance Document (ECB, 2003).

[4] Concentrations in soil are shown for standard soil (10% organic matter and 25% clay).

[5] Standards for land-application of biosolids (40 CFR Part 503):

Ceiling concentration—Maximum permissible concentration in bulk sewage sludge or sewage sludge sold or given away in a bag or other container to be applied to the land.

Cumulative Application Limit—Maximum permissible cumulative loading rate.

Alternate Pollutant Limit—Maximum permissible concentration in the sewage sludge; all alternate pollutant limits (for eight other pollutants) must be met simultaneously.

Recent effects studies on aquatic and terrestrial species (De Schamphelaere *et al*., 2010; McGrath *et al*., 2010a; van Gestel *et al*., 2010) fill some of the data gaps and indicate that these MPCs are overly conservative. For example, De Schamphelaere *et al*. (2010) evaluated existing aquatic data and generated new data to derive an aquatic Hazard Concentration (HC) that is protective of 95% of the aquatic species using accepted regulatory guidance, *i.e.*, the European Union's Technical Guidance Document on Risk Assessment (ECB, 2003). Based on a species sensitivity distribution of the NOECs and/or EC10s for the most sensitive aquatic species, an aquatic HC of 38.2 mg/L was derived, which is orders of magnitude greater than the Dutch MPC of 30 µg/L, but only slightly lower than the Dutch $\mathrm{SRC}_{\mathrm{ECO}}$ of 54 mg/L.

Similar to surface water MPCs, a soil MPC of 1.3 mg Mo/kg for soil (Table 4-6) is conservative because it is based on 100% protection (*i.e.*, no effects at all). To derive the soil MPC, a safety factor of 100 was applied to the NOEC (76 mg/kg) for urease activity inhibition and added to the 90th percentile background soil concentration in the Netherlands (0.5 mg/kg). The results of the McGrath *et al*. (2010a) and van Gestel *et al*. (2010) studies indicate the conservative nature of the Dutch standards. In 10 soils with wide-ranging properties, the NOECs and/or EC10s for several species of terrestrial plants and invertebrates varied widely (McGrath *et al*., 2010a; van

Gestel *et al*., 2010) and, generally, were significantly greater than the Dutch screening criteria in several cases. Like the Dutch criteria, the NOAA SQuiRTs soil screening levels were developed using conservative assumptions and limited data. In effect, soil Mo concentrations below these values can be used to indicate an absence of any adverse effects, but soil concentrations above these values do not necessarily indicate the presence of an ecological problem.

In 1994, US EPA promulgated risk-based values for the permissible levels of Mo in biosolids of 75 mg/kg in sludge (US EPA, 2007). However, most Mo standards were withdrawn following a legal challenge for reassessment and have not been redeveloped (40 CFR Part 503) (US EPA, 2007). In 2001, O'Connor *et al*. (2001) proposed new standards for Mo in biosolids (Table 4-6). They relied on newer and more reliable data (on biosolids Mo concentrations, background soil concentrations, and forage uptake coefficients from field studies using biosolids) and improved the algorithm to account for diet contribution from biosolids-receiving pastures/land and Mo leaching from soil. The resulting cumulative biosolids Mo application limit (RPc) was 40 kg/hectare, and an alternate concentration of Mo in biosolids of 40 mg/kg was proposed.

4.7 Ecological Benchmark Toolbox

Government and private websites and reports provide useful information on Mo ecotoxicity and ecological risk assessment. The list below presents some key resources.

- Cleanup Levels for Hazardous Waste Sites (US EPA examples)
    - Website: http://www.epa.gov/superfund/health/conmedia/soil/index.htm; http://water.epa.gov/drink/contaminants/index.cfm
    - US EPA soil screening guidance documents and drinking water guidance documents.
- Ecological Benchmark Tool (University of Tennessee, 2007)
    - Website: http://rais.ornl.gov/tools/eco_search.php
    - This website provides a searchable database with a comprehensive set of ecotoxicological screening benchmarks for surface water, sediment, and surface soil applicable to a range of aquatic organisms, soil invertebrates, and terrestrial plants. Also provided are the links to supporting technical reports from which the benchmarks were obtained.
- Ecological Risk Analysis: Guidance, Tools, and Applications (ORNL, 2003)
    - Website: http://www.esd.ornl.gov/programs/ecorisk/contaminated_sites.html
    - This page contains information that can be used to conduct screening and baseline ecological risk assessments at hazardous waste sites.
- The Ecotoxicological (ECOTOX) Database (US EPA, 2007)
    - Website: http://cfpub.epa.gov/ecotox/quick_query.htm
    - This searchable database provides aquatic and terrestrial life toxicity data and the associated primary literature references, and can be searched by chemical name.
- IMOA Database of Molybdenum in Human Health and the Environment
    - Website: http://www.imoa.info/HSE/environmental_data/database.html

  - IMOA’s database provides excerpts, summaries, and data from studies and resources pertaining to environmental effects and exposures of Mo.

- Molybdenum Consortium (Formed for REACH Registration)
  - Website: http://www.molybdenumconsortium.org/
  - This is a membership-only website for parties involved in registration of Mo compounds under REACH.
- NOAA’s SQuiRTs (Buchman, 2008)
  - Website: http://response.restoration.noaa.gov/book_shelf/122_NEW-SQuiRTs.pdf
  - SQuiRTs provide ecological screening levels compiled from various sources for Mo in soil, surface water, and groundwater.

5
GEOCHEMISTRY AND FATE AND TRANSPORT

This chapter focuses on the geochemistry and fate and transport of Mo in the environment. The basic chemical and physical properties are presented in Section 5.1, followed in Section 5.2 by a discussion of solid-phase Mo in minerals, soil, sediment, and coal. Section 5.3 describes the aqueous geochemistry of Mo, including speciation, dissolution-precipitation, adsorption-desorption, and oxidation-reduction. Section 5.4 discusses Mo fate and transport, including modeling.

As described in greater detail within this chapter, the most common mineral forms of Mo are molybdenite and wulfenite. It is a chalcophile element and is often associated with sulfidic sedimentary environments. In coal and black shales, Mo is associated with both pyritic and organic fractions (Querol *et al*., 1996; Eskanazy, 2009; Wang *et al*., 2009). Mo is mobilized by oxygenic weathering of black shales.

In oxic waters, molybdate is the principal form of Mo (Ryzhenko, 2010). Similar to other oxyanions such as Cr (VI) and Se (VI), molybdate is relatively mobile in groundwater (Hem, 1985; US EPA, 2005). Mo adsorption on both minerals and organic matter is highly pH-dependent, with peak adsorption at $\text{pH} < 5$ and limited adsorption above a pH of 8 (Goldberg and Forster, 1998). Increases in soil water pH or dissolution of oxide phases can readily mobilize Mo. In alkaline conditions, Mo behaves conservatively (*i.e.*, is mobile), and its dissolved concentration may be controlled by precipitation reactions (Wang *et al*., 1994; Meima *et al*., 2002; Essington, 1992). The environmental chemistry of Mo has been well described in the literature, but there have been fewer attempts to model its environmental fate and transport.

5.1 Basic Chemical and Physical Properties

Mo is a transition metal located in group 6 of the periodic table along with chromium and tungsten. In its pure state, Mo occurs as a silvery white metal (Cotton and Wilkinson, 1988). There are seven naturally occurring isotopes of Mo: 92 (natural abundance 14.84%), 94 (9.25%), 95 (15.92%), 96 (16.68%), 97 (9.55%), 98 (24.13%), and 100 (9.63%). Mo in compounds exists primarily in +4 and +6 oxidation states, but it may also form compounds with -2, 0, +1, +2, +3, and +5 oxidation states (Cotton and Wilkinson, 1988). The most common dissolved form of Mo is the molybdate oxyanion (Ryzhenko, 2010). Table 5-1 provides several additional chemical and physical properties for Mo.

Table 5-1
Basic Chemical and Physical Properties of Molybdenum

Property	Value	Property	Value
Symbol	Mo	Liquid Density (melting point)	9.33 g/cm^3
Atomic Number	42	Melting Point	2896 K; 2623°C
Atomic Mass	95.94 g/mol	Boiling Point	4912 K; 4639°C
Chemical Series	Transition metal	Heat of Fusion	37.48 kJ/mol
Valence States	6, 5, 4, 3, 2, 1, 0, -1, -2	Heat of Vaporization	617 kJ/mol
Room Temperature Phase	Solid	Heat Capacity	24.06 J/mol K
Solid Density (25°C)	10.29 g/cm^3		

5.2 Solid-Phase Geochemistry

5.2.1 Molybdenum Minerals

Mo is the least abundant of the biologically essential trace elements in soil. The mean concentration of Mo in the upper continental crust, from which soil is formed, is 1.4 mg/kg (Wedepohl, 1995). EPRI (2010) reported a range of Mo concentrations in rocks and minerals from < 0.05-640 mg/kg, with a median value of 1.6 mg/kg. There are over 50 identified Mo-bearing minerals, but the most common Mo minerals and primary ore sources are molybdenite and wulfenite. Molybdenite forms from high-temperature hydrothermal fluids associated with porphyry deposits (Smith *et al*., 1997). Wulfenite is usually found in the oxidized zone of mineral deposits containing Mo and lead (Smith *et al*., 1997). Mo is also associated with uranium ore deposits (Dahlkamp, 2009). It can be found in both hydrothermal uranium deposits and sedimentary-hosted uranium deposits associated with changes in redox conditions (Dahlkamp, 2009).

5.2.2 Molybdenum in Soil and Sediment

Pure-phase Mo minerals are generally not found in oxic soil environments. Instead, solid-phase Mo is commonly found adsorbed to iron or aluminum oxides, clay minerals, and/or organic matter such as humics and tannins (Goldberg *et al*., 1996; Wichard *et al*., 2009). In oxic sediment, Mo is often associated with ferromanganese oxides (Bertine and Turekian, 1973; Emerson and Huested, 1991; Morford and Emerson, 1999). In anoxic sediments and shales, Mo is associated with the iron sulfide pyrite (Vorlicek *et al*., 2004), and Mo concentrations in anoxic sediments can be as high as 140 mg/kg (Zheng *et al*., 2000).

5.2.3 Molybdenum in Coal

Coal contains minor amounts of many trace elements that can be incorporated into the coal at the time of deposition or by post-depositional changes, including by mineralizing fluids (Finkelman, 1995). The concentrations of trace elements in coal can vary widely, even within the same coal bed, and may be associated with clay mineral, sulfate, organic, or pyritic fractions (Finkelman, 1995).

The United States Geological Survey (USGS) Coal Quality Database contains 7,430 analyses of Mo in domestic coal samples (USGS, 1998a). Mo concentrations in these samples range from 0.03-280 mg/kg, with a median concentration of 1.7 mg/kg (Figure 5-1). There is not a significant difference in the median concentrations of Mo by coal type, which range from 1.3-2.1 mg/kg (Figure 5-2). There is a slightly wider range in median values, from 1.1-3.0 mg/kg, when coals are categorized by US coal province of origin (Figure 5-3). The higher Mo in interior coals may be related to its generally higher sulfur content (see Figure 5-4 and Section 5.2.3.1).

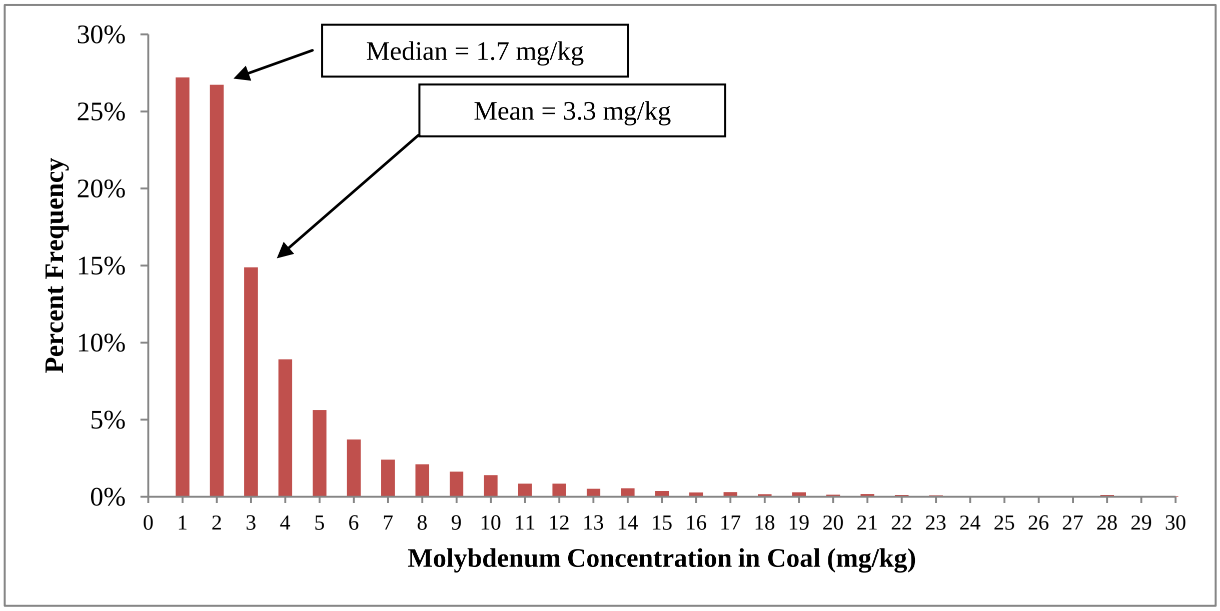


Figure 5-1
Molybdenum Concentration Distribution in Domestic Coal (Histogram)

Notes: Figure represents 99% of the analyses. The highest concentration samples were not plotted. Data from USGS, 1998a.

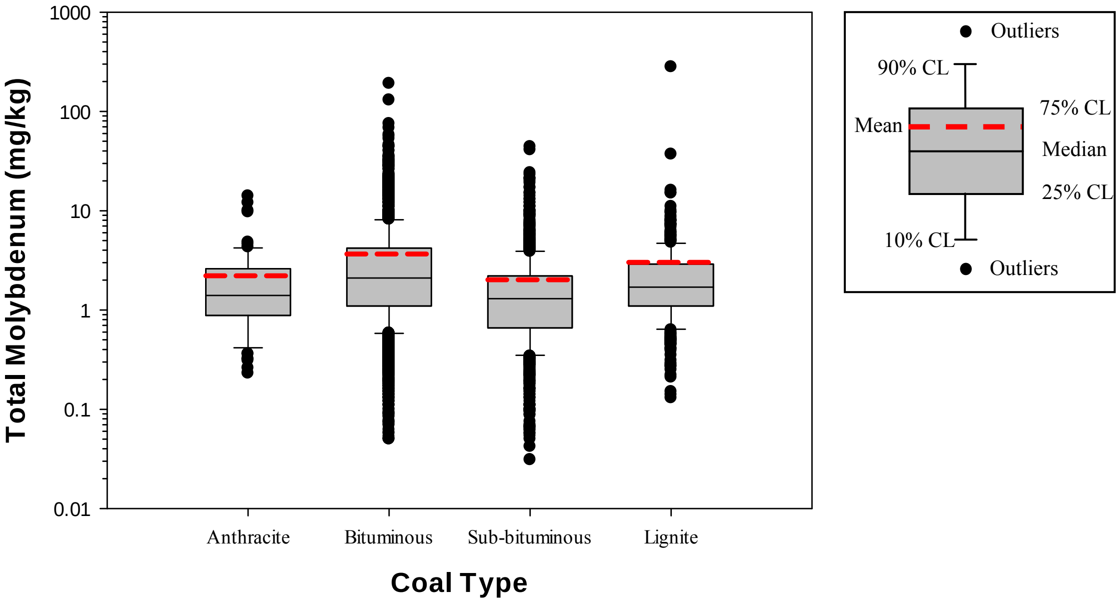


Figure 5-2
Comparison of Molybdenum Concentrations in Coal by Type

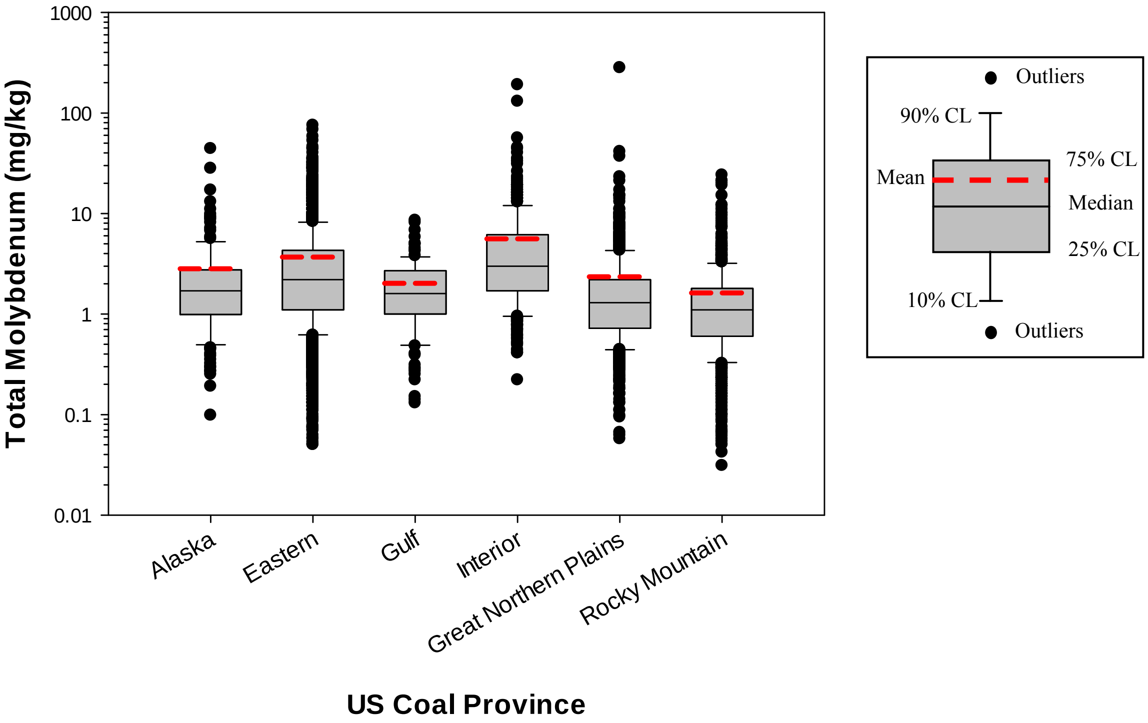


Figure 5-3
Comparison of Molybdenum Concentrations by US Coal Province

Note: Data for Figures 5-2 and 5-3 from USGS, 1998a.

5.2.3.1 Mode of Occurrence

While Mo appears to be associated with both organic and sulfide phases of coal based on leaching studies, x-ray and microprobe analysis have not been performed to confirm this, and there is currently no scientific consensus on this issue (Finkelman, 1995). Coal leaching studies (Querol *et al*., 1996; Eskanazy, 2009; Wang *et al*., 2009) show that Mo is optimally removed under pH conditions that target organic and sulfide-bound elements. Further, Mo's chalcophile tendencies lead to its association with pyrite (FeS_2). In the US, higher-sulfide coals from the Appalachian and Interior regions appear to have higher mean Mo concentrations than coals from other coal regions (Figure 5-4). Pyrites separated from eastern Canadian coal have concentrations of Mo ranging from 35-160 mg/kg (Zodrow and Goodarzi, 1993; Finkelman, 1995; Goodarzi, 2002).

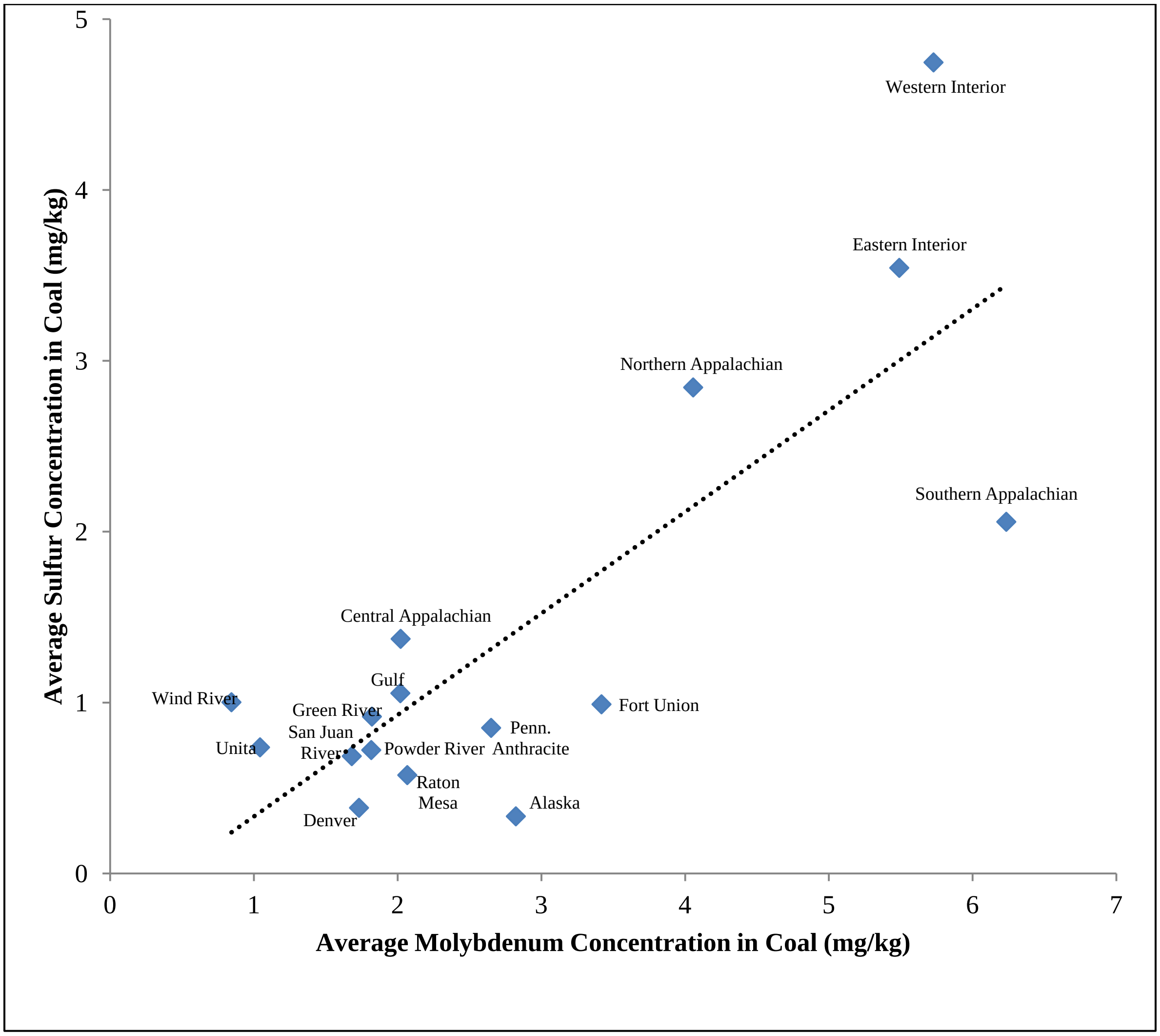


Figure 5-4
Molybdenum Versus Sulfur Concentrations in Coal by US Coal Regions

Note: Data from USGS, 1998a.

5.3 Aqueous Geochemistry

As discussed in Chapter 2, the concentration of Mo in water varies widely. Fresh surface waters and groundwater contain low levels of Mo that are typically below detection (approximately 5 μg/L Mo or less), but concentrations can increase with alkalinity up to hundreds of μg/L (Ryzhenko, 2010; Hem, 1985; WHO, 2003). Oxic seawater average Mo concentrations are higher, at about 10 μg/L (Hem, 1985; Manheim and Landergren, 1978; Ryzhenko, 2010; Bertine and Turekian, 1973). The factors controlling Mo aqueous geochemistry are discussed below.

5.3.1 Speciation

5.3.1.1 Redox State (Eh-pH Diagram)

Eh-pH diagrams represent the equilibrium speciation of a compound under a defined set of conditions (*i.e.*, “redox state”). As such, they are a useful theoretical tool for predicting speciation. It should be recognized, however, that most groundwater systems exist in a state of redox disequilibrium (Langmuir, 1997) due to kinetic or biologic control of reactions. Therefore, while thermodynamically favored, equilibrium may never be reached in some instances.

Ryzhenko (2010) calculated a recent Eh-pH diagram for the Mo-O-H-S system (Figure 5-5), which shows that the molybdate ion dominates Mo aqueous speciation except under low pH (< 4) and anoxic conditions. Molybdate is the most environmentally significant form of Mo (VI) in surface waters and soil solutions (De Schamphelaere *et al*., 2010). Hydrogenated molybdate species ($HMoO_4^-$ and H_2MoO_4) become important at lower pH, below their appropriate acid dissociation constants (pK_a). The acid dissociation constants of molybdate are in the range of pH 2-5, but there is no consensus in the literature (Table 5-2).

Under anoxic conditions, molybdenite is the thermodynamically favored species. The solubility of molybdenite is driven by the reaction:

$$MoS_2 + 12\ H_2O = MoO_4^{2-} + 2SO_4^{2-} + 24\ H^+ + 18e^-$$

Molybdenite dissolution is thought to be a source of Mo during weathering. However, although thermodynamically predicted, molybdenite precipitation rarely occurs under aqueous conditions below 300°C (Helz *et al*., 1996). Redox reactions are more likely than acid dissociation to be kinetically hindered. Molybdenite has not been identified in black shales or anoxic sediments (Vorlicek *et al*., 2004; Helz, *et al*., 1996).

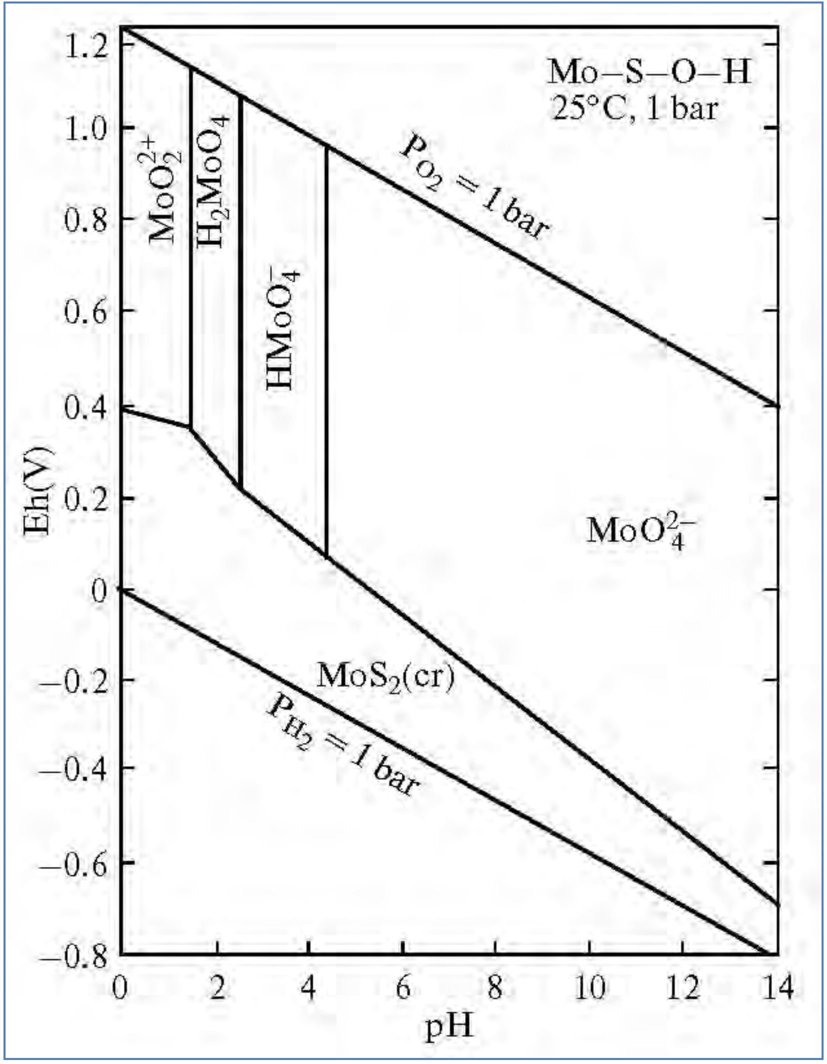


Figure 5-5
Eh-pH Diagram for the Mo-O-H-S System

Notes: *At 25 °C, concentration of Mo is 10^{-8} M and S 10^{-3} M.*
From Ryzhenko, 2010.

Table 5-2
Molybdate Acid Dissociation Constants

Reaction	pK$_a$		
	Ryzhenko, 2010	Cruywagen, 1999	Lindsay, 1979
$H_2MoO_4 + 2H^+ = MoO_2^{2+} + 2H_2O$	1.40	N/A	N/A
$H_2MoO_4 = HMoO_4^- + H^+$	2.45	3.74	4.00
$HMoO_4^- = MoO_4^{2-} + H^+$	4.40	3.47	4.24

Note: N/A = not applicable.

5.3.1.2 Speciation with Hydrogen Sulfide

Another factor that influences Mo aqueous speciation is the aqueous concentration of hydrogen sulfide (H_2S). At H_2S concentrations > 10 mg/L, thiomolybdates have been shown to be stable in near-neutral to alkaline waters (Erickson and Helz, 2000). These species do not undergo a redox transition but are the result of replacement of the molybdate oxygen atoms with sulfide atoms, with tetrathiomolybdate as the end product: $MoO_4^{2-} \rightarrow MoO_3S^{2-} \rightarrow MoO_2S_2^{2-} \rightarrow MoOS_3^{2-} \rightarrow MoS_4^{2-}$ (Erickson and Helz, 2000; Ryzhenko, 2010). Tetrathiomolybdates are soft ligands and rapidly bind with other transition metals and particles. Tetrathiomolybdate has an extremely high affinity for copper, and it will also bind other trace elements (iron, zinc) to a lesser degree. Helz *et al*. (1996) have proposed the concept of a "sulfide switch" to describe this behavior, in which HS^- transforms the behavior of aqueous Mo from that of a conservative element to that of a particle reactive element. This mechanism removes the role of reduction in Mo scavenging in favor of forming Mo bonds with metals and organics via S bridges.

5.3.1.3 Speciation with Dissolved Organic Matter

Mo is not bound by most organic compounds, but there is some evidence that Mo may be associated with humic acids and tannins. Mo has the highest affinity for catechol groups such as those found in azotochelin, a compound produced by nitrogen-fixing soil bacteria that aids in the uptake of iron and Mo (the two metals required for nitrogen fixation). Tannins contain catechol groups that have been shown to bind Mo in leaf litter extract and also may bind Mo in the dissolved phase (Wichard *et al*., 2009). The interaction between Mo and organic matter is discussed further below.

5.3.2 Solid-Liquid Partitioning

As described previously, the aqueous concentration of Mo is affected by interaction with solid phases through the processes of precipitation-dissolution and adsorption-desorption. These processes are in turn influenced by dissolved phase speciation.

5.3.2.1 Precipitation-Dissolution

Many Mo minerals are highly soluble under neutral to basic conditions (see Table 5-3). For example, molybdenite is stable in acidic conditions but, under neutral or basic conditions, it is weathered and oxidized, mobilizing Mo as molybdate. As discussed above, molybdenite precipitation is kinetically hindered in most soil environments. While molybdate reduction and precipitation as molybdenite has long been thought to be the ultimate sink for Mo in anoxic sediments, empirical measurements have failed to identify molybdenite in anoxic sediments (Bostick *et al*., 2003; Helz *et al*., 1996). X-ray adsorption analyses of Mo-rich shales and sediments and in laboratory experiments with pyrite have found Mo absorbed to iron phases rather than precipitated as molybdenite (Helz *et al*., 1996; Bostick *et al*., 2003). These data suggest that adsorption of thiomolybdates, rather than direct precipitation as molybdenite, may be the mechanism for Mo removal in anoxic sediments. This has implications for the ease of remobilization of Mo in sediments. Adsorbed species are generally remobilized more easily than the less soluble molybdenite upon reoxygenation (Helz *et al*., 1996).

Table 5-3
Molybdenum Mineral Solubility

Mineral	Formula	Solubility (mg/L) 25°C pH 7.0	log Solubility Constant (K_{sp})
Ferrous Molybdate	$Fe(III)_3(MoO_4)_2$	20	NR
Ferrimolybdite	$Fe(II)MoO_4$	15	-7.76
Powellite	$CaMoO_4$	10	-7.02 to -8.51
Molybdite	MoO_3	2.6	-4.47
Molybdenite	MoS_2	0.2	NR
Wulfenite	$PbMoO_4$	Relatively Insoluble	-16

Notes: NR = not reported.

Source: Essington (1990); Wang et al. (1994).

Lindsay (1979) gave the following sequence for the solubility of Mo minerals in soils: $CuMoO_4 > ZnMoO_4 > MoO_3 > H_2MoO_4 > CaMoO_4 > PbMoO_4$. Wulfenite is an extremely stable Mo solid (log $K_{sp} = -16$). In environments where a source of lead is available, the formation of wulfenite may be a sink for Mo. Wang *et al*. (1994) investigated Mo solubility in soil from a surface coal mine, soil near a coal mine, and native soil in the Powder River Basin. These results suggested that, when corrected for the effect of fulvic acid complexation of lead, these soils were approaching saturations for wulfenite, implying that dissolved Mo concentrations in these soils may be controlled by wulfenite precipitation. In areas without a source of lead, powellite has been predicted to be the controlling phase for Mo in alkaline materials. Powellite is slightly soluble, with an estimated log K_{sp} ranging from -7.02 to -8.51 (Essington, 1990). Powellite has been suggested to be the controlling phase in alkaline municipal solid waste leachates (Meima *et al*., 2002). In natural waters with elevated Fe (II) concentrations, $Fe(II)MoO_4$ precipitation may occur; however, elevated Fe (II) is thermodynamically favored only at pH < 6 (Stumm and Morgan, 1981), a region where, as discussed below, significant Mo adsorption is expected.

5.3.2.2 Adsorption/Desorption

Mo adsorption is highly pH-dependent. Adsorption on all minerals investigated shows maximum Mo adsorption at $pH < 5$ (Goldberg *et al*., 1996; Goldberg and Forster, 1998). Mo behaves conservatively in alkaline seawater (Emerson and Huested, 1991) and groundwater aquifers (Hodge *et al*., 1996). The pH effect on molybdate adsorption is likely related to the pH-dependent surface charges common in oxyhydroxides. Many oxyhydroxides have isoelectric points (IEPs, the pH at which oxide surface charge transitions from positive to negative) in the pH range of 4-8, where Mo adsorption drops off rapidly (Table 5-4). In addition, it is common for anions to exhibit peak adsorption that coincides with their pK_a values; for Mo, this occurs near pH 4 (Barrow, 1977, as cited in Chappell and Peterson, 1977).

Competing ions can limit Mo adsorption by soils and minerals. A variety of oxyanions (SO_4^{2-}, PO_4^{2-}, SeO_4^{2-}, WO_4^{2-}, SiO_4^{2-}, AsO_4^{2-}) have been investigated to determine their effect on Mo adsorption. Generally, oxyanions compete with each other for adsorption sites, and concentration ratios between oxyanions can play an important role in determining adsorption. The adsorption affinity for oxyanions on a volcanic soil was determined to be $PO_4^{2-} > SeO_3^{2-} > MoO_4^{2-} \geq AsO_4^{2-} > > SeO_4^{2} \geq CrO_4^{2-}$ (Saeki, 2008). Equimolar concentrations of phosphate, arsenate, selenate, or tungstate have been shown to depress Mo uptake on aluminum and iron oxides, but silicate had little effect (Xu *et al*., 2006; Goldberg, 2009). The presence of sulfate depresses Mo uptake on aluminum oxides (Goldberg, 2009) but not iron oxides (Xu *et al*., 2006), even at concentration ratios more reflective of natural systems (1:100). In soil, sulfate has been found to depress Mo adsorption occasionally, but not consistently (Goldberg *et al*., 1996). Phosphate decreased Mo adsorption in all soil tested (Goldberg *et al*., 1996; Goldberg and Forster, 1998).

The solid characteristics of the aborbent, including the surface area (S_A) and site density (N_S), describe the potential sorption capacity of the solid. These values set a limit on the total amount of Mo adsorption that can take place. Adsorption of trace elements can occur either by outer-sphere complexation, driven by electrostatic attraction between ions and the mineral surface, or inner-sphere complexation, which includes the formation of coordinate bonds between the ion and the mineral surface. Inner-sphere complexation tends to be stronger and less easily reversible than outer-sphere complexation. Table 5-4 describes properties of some Mo sorbents, which are discussed further below. Ferrihydrate shows the greatest number of potential sites for Mo adsorption on a per gram basis [adsorption sites available (sites/g) = N_S (sites/nm^2) x 10^{18} (nm^2/m^2) x S_A (m^2/g)], followed by fresh manganese oxides. These are also considered the two most important phases for Mo adsorption in nature (Goldberg *et al*., 1996). Appendix A provides more detail on specific Mo sorbents.

Table 5-4
Properties of Molybdenum Sorbents

Type	Solid	IEP (pH)	S_A (m^2/g)	N_S (sites/nm^2)
Fe/Mn Oxides and Oxyhydroxides	Fe_2O_3 (Hematite)	4.2-6.9	1.8	22-55
	$Fe(OH)_3$ (Ferrihydrate)	8.5-8.8	250-600	20
	FeOOH (Goethite)	5.9-6.7	45-169	2.6-16.8
	MnO_2 (Birnessite)	4.5	290 (fresh), 143 (weathered), 180 (natural)	18 (fresh), 2 (weathered)
Al Oxides and Clay Minerals	$Al(OH)_3$ (Gibbsite)	9.4	120	2-12
	$Al_2Si_2O_5(OH)_4$ (Kaolinite)	2.9	9.1-19.3	NR
Pyrite	FeS_2 (Pyrite)	7.6	NR	NR

Notes: S_A = surface area; N_S = number of adsorption sites; NR = not reported; IEP = isoelectric point.

Sources: Langmuir, 1997; EPRI, 2006a.

5.4 Environmental Fate and Transport in Groundwater

To summarize, Mo mobility in soils and groundwater is primarily controlled by adsorption-desorption and precipitation-dissolution reactions. The key factors controlling Mo mobility are groundwater pH, redox conditions, and the presence of competing oxyanions. Mo adsorption on both minerals and organic matter is highly pH-dependent, with peak adsorption at $pH < 5$ and limited adsorption above pH 8. Phosphate and several other oxyanions will depress Mo adsorption. Mo desorbs from most soils with a change in pH or competing ion concentrations (phosphate in particular). Permanent fixation of Mo requires anoxic conditions and pyrite. Thiomolybdates, formed by the replacement of the molybdate oxygen with sulfur when H_2S concentrations are elevated, appear to be irreversibly scavenged by pyrite. This mechanism has been proposed to sequester Mo in anoxic sediments. In neutral to alkaline conditions, Mo adsorption is minimal and Mo dissolved concentrations may be controlled by precipitation. In the presence of excess lead, precipitation of wulfenite has been shown to control dissolved Mo concentrations in soils near coal mines (Wang *et al*., 1994). In the absence of elevated lead concentrations, Mo dissolved concentrations may be controlled by powellite precipitation, resulting in potential equilibrium Mo concentrations on the order of 10 mg/L (Meima *et al*., 2002; Essington, 1992).

5.4.1 Distribution Coefficients

Soil-water bulk distribution coefficients (K_d) are used to estimate the mobility of an element in groundwater. The K_d is the ratio of the mass of a constituent adsorbed to the solids over the mass in solution, and it is generally reported as L/kg. When the K_d approaches zero, the constituent behaves conservatively and remains in the dissolved phase. It will travel at the same velocity as groundwater. When the K_d is above zero, the constituent reacts with the solid matrix and travels at a rate slower than the velocity of the groundwater. For example, a constituent with a K_d of approximately 2 L/kg will travel at approximately one-tenth the velocity of groundwater (EPRI, 2006a).

Relatively few experimental bulk distribution coefficients for Mo have been reported in the literature. After an extensive literature survey, US EPA (2005) found only eight reported values, with pH conditions ranging from 4-10. The median K_d was 12.6 L/kg, with a reported range of 0.6-501 L/kg. Mo distribution coefficients are similar to other oxyanions, all of which are highly mobile in groundwater under neutral to alkaline conditions (Table 5-5).

Table 5-5
Experimental Metal-Soil Water Distribution Coefficients

Element	Distribution Coefficient (K_d)				Median Retardation Factor (R_d)	Median Velocity Relative to Groundwater[1] (V_c/V_{gw})
	Median (L/kg)	Minimum (L/kg)	Maximum (L/kg)	N		
As	2512	2.0	19900	22	15500	0.00006
Cr (III)	7940	10.0	50100	43	49000	0.00002
Cr (IV)	12.6	0.2	1990	24	79	0.013
Mo	12.6	0.6	501	8	79	0.013
Se	10.0	0.5	251	23	63	0.016
V	NA	12.6	501	2	NA	NA

Notes: [1] $V_c/V_{gw} = 1/R_d = 1 + K_d$ * Bulk Density / Porosity; R_d = retardation coefficient; K_d = distribution coefficient. Assumes a bulk density of 1.85 kg/L and porosity of 0.3.

Source: US EPA (2005).

K_d values can also be estimated for specific soil and groundwater conditions using aqueous speciation models. For the Human and Ecological Risk Assessment of Coal Combustion Wastes (US EPA, 2010a), US EPA used MINTEQA2 to model adsorption of groundwater constituents to soil for a range of conditions representing coal combustion leachate (US EPA, 2001). The resulting K_d values were all 2 L/kg or below (Table 5-6), suggesting that the US EPA model characterizes Mo as relatively mobile in groundwater at CCP sites.

Table 5-6
Distribution Coefficients Calculated for Coal Combustion Waste Leachate

Leachate Source	Land Fill/Surface Impoundment	Soil Zone	Distribution Coefficients (K_d)		
			10% CL (L/kg)	Mean (L/kg)	90% CL (L/kg)
Ash	LF	Saturated	< 0.0001	0.0018	0.37
	SI	Saturated	< 0.0001	0.0043	0.24
	LF	Unsaturated	0.023	0.34	2.0
	SI	Unsaturated	< 0.0001	0.16	1.3
Ash & Coal Refuse	LF	Saturated	< 0.0001	0.0025	0.27
	SI	Saturated	< 0.0001	0.011	0.31
	LF	Unsaturated	< 0.0001	0.21	2.0
Fluidized Bed Combustion	LF	Saturated	< 0.0001	0.0001	0.027
	LF	Unsaturated	< 0.0001	0.23	1.9

Notes: Source: US EPA, 2010a.
CL= Confidence Limit

5.4.2 Fate and Transport Models

Reactive transport models incorporate adsorption-desorption reactions via empirical relationships or surface complexation models (SCMs) that represent the adsorption process. Empirical models, which include a bulk K_d based on Langmuir and/or Freundlich isotherm equations, are more commonly incorporated into transport models, but they do not address the effects of variable chemical conditions like pH or other dissolved constituents. Most US EPA or USGS-supported transport codes use empirical relationships to describe adsorption (Goldberg *et al.*, 2007). SCMs describe adsorption as a process analogous to aqueous-phase reactions. Examples of SCMs applied to Mo adsorption, and references for further information on these models, include:

- Constant capacitance model (CCM): Goldberg *et al.*, 1996, 2002; Goldberg and Forster, 1998; Saripalli *et al.*, 2002
- Diffuse layer model (DLM): Dzombak and Morel, 1990; Stollenwerk, 1995; Gustafsson, 2003
- Triple layer model (TLM): Goldberg and Forster, 1998; Wu *et al.*, 2001
- CD-MUSIC model: Gustafsson, 2003; Xu *et al.*, 2006

SCM models may require a large number of variables to describe the adsorption process. These variables may not be known for a field site, which can make it difficult to incorporate SCMs into transport modeling. However, several researchers who have used SCMs to predict Mo adsorption on suites of soil samples have found that Mo adsorption can be described successfully using a relatively limited number of parameters:

- Goldberg *et al*. (2002) used the CCM to predict molybdate adsorption by soils. Mo adsorption was predicted successfully in 36 different soils by using four independently measured soil parameters: cation exchange capacity, OC content, inorganic carbon content, and iron oxide content.
- Dijkstra *et al*. (2009) used a multi-surface sorption model to predict trace metal leaching from a variety of industrial soils. This approach included aqueous speciation in combination with sorption to organic matter, iron/aluminum (hydr)oxides, and clay. The model relied on total available metal concentrations, concentrations of reactive surfaces (organic matter, iron/aluminum (hydr)oxides and clay), pH, and redox potential to estimate Mo leaching.
- Rodrigues *et al*. (2010) used a multiple regression analysis to compare trace metal concentrations measured in a suite of 136 Portuguese soils with those predicted using empirical Freundlich isotherms combined with a mechanistically based speciation model (ORCHESTRA with the NICA-Donnan model). They found that available Mo could be described successfully by total reactive metal content, pH, OC concentration, and clay concentration.

In one of the few successful applications of a field-scale SCM, Stollenwerk (1995) used a DLM calibrated to simulate molybdate transport in soil columns to predict Mo transport in a shallow sandy aquifer. This work was part of a large-scale natural gradient tracer test performed on Cape Cod, Massachusetts, where molybdate was used as a reactive tracer (in comparison to bromide, the non-reactive tracer). The Mo concentration distribution was asymmetric, with the maximum concentrations found at the leading edge with a long dilute tail. This is consistent with the understanding of molybdate rapid adsorption to soil, followed by a slow desorption. Stollenwerk (1995) identified pH, phosphate, and, to a lesser extent, sulfate concentrations as the primary factors affecting molybdate adsorption. Mo adsorption was the highest at the surface (which had low pH and phosphate and sulfate concentrations) and decreased at depth (which had higher pH and phosphate and sulfate concentrations). The DLM model was limited in its ability to simulate mass transfer, and the MINTEQ model used for chemical speciation was limited in its ability to account for reaction kinetics. The main results of these limitations appeared to be under-prediction of the amount of time it took for Mo to be removed from an aquifer.

More recently, Carroll *et al*. (2006) used the PHREEQC model to predict Mo transport in bio-solid amended, alkaline, agricultural soil. The K_d of Mo in the control and bio-solid amended soils was determined experimentally to be 0.29 L/kg and 1.24 L/kg, respectively. The adsorption of Mo was predicted using the DLM model, similar to Stollenwerk (1998). The Mo adsorption was higher in the amended soils and agreed with experimental results. Adsorption was rate-limited and reversible. The results showed that Mo was only temporarily adsorbed when applied to alkaline agricultural soils and was rapidly leached (Carroll *et al*., 2006).

6
COAL COMBUSTION PRODUCTS

This chapter discusses the occurrence of Mo in CCPs and leaching of Mo at CCP disposal sites.

6.1 Molybdenum Concentrations in Coal Combustion Products

Like coal, CCPs also contain minor amounts of trace elements, including Mo, the concentration of which varies depending on the CCP type. Mo volatilizes and is carried along with flue gas after coal is combusted (Vories and Throgmorton, 2002; Querol *et al*., 1995). Partial condensation in the particulate collection and FGD systems results in the capture and recovery of Mo in fly ash and FGD residuals (Querol *et al*., 1995).

6.1.1 Concentrations

This section describes the concentration of Mo in CCPs based on the EPRI (2011a) dataset. The EPRI dataset consists of 227 CCP samples collected from 76 power plants categorized into the following CCP types: fly ash, bottom ash, mixed coal ash (fly ash with bottom ash), FGD scrubber sludge (FGD SS) solids (calcium sulfite hemihydrate from wet scrubbers with inhibited or natural oxidation), and FGD gypsum (calcium sulfate dihydrate from wet scrubbers with forced oxidation). The concentration of Mo in these samples ranged from 0.04-236 mg/kg, with a mean of 19.2 mg/kg and a median of 11.2 mg/kg.

Table 6-1 presents summary statistics of Mo concentrations in the different CCP types. This table shows both discrete sampling results for each CCP type, as well as plant average data where all of the discrete samples collected from each plant for the stated CCP type have been averaged into a single value. Figure 6-1 depicts these plant-averaged concentrations by CCP type. As can be seen from Table 6-1 and Figure 6-1, the highest median and maximum concentrations of Mo are associated with fly ash and mixed coal ash, followed by bottom ash and FGD SS, then FGD gypsum. Figure 6-2 (a-e) displays further detail of the EPRI (2011a) dataset, showing the range in Mo concentration from discrete CCP samples collected at individual plants. Based on the EPRI (2011a) dataset, ash samples typically have concentrations of approximately 10-20 mg/kg Mo, but can range up to 100 mg/kg or more in some instances. The Mo concentration in FGD SS typically ranges from about 1 to10 mg/kg, and FGD gypsum samples typically have concentrations < 1 mg/kg Mo.

Table 6-1
Molybdenum Concentration in CCPs – Summary Statistics

CCP Type	# of Discrete Samples	# of Utility Plants	# of Non-Detects	Discrete Sample Data (mg/kg)[2]			Plant Average Data (mg/kg)[2]		
				Mean	Median	Range	Mean	Median	Range
Fly Ash	81	50	0	26.2	16.0	2.0-236.0	28.4	18.5	4.5-138.9
Bottom Ash	38	30	2	13.5	11.0	0.9-45.5	13.7	11.2	0.9-45.5
Mixed Coal Ash[1]	52	7	22	29.6	15.9	0.9-140	27.4	25.2	1.1-53.9
FGD SS[3]	22	10	9	7.1	5.6	0.6-52.6	10.2	7.4	0.8-52.6
FGD Gypsum	34	29	0	0.7	0.6	0.044-3.1	0.7	0.6	0.044-3.1

Notes: *[1] Mixed coal ash is a mixture of bottom ash and fly ash.*
[2] Non-detects included at one-half the reported detection limit.
[3] FGD scrubber sludge (calcium sulfite)

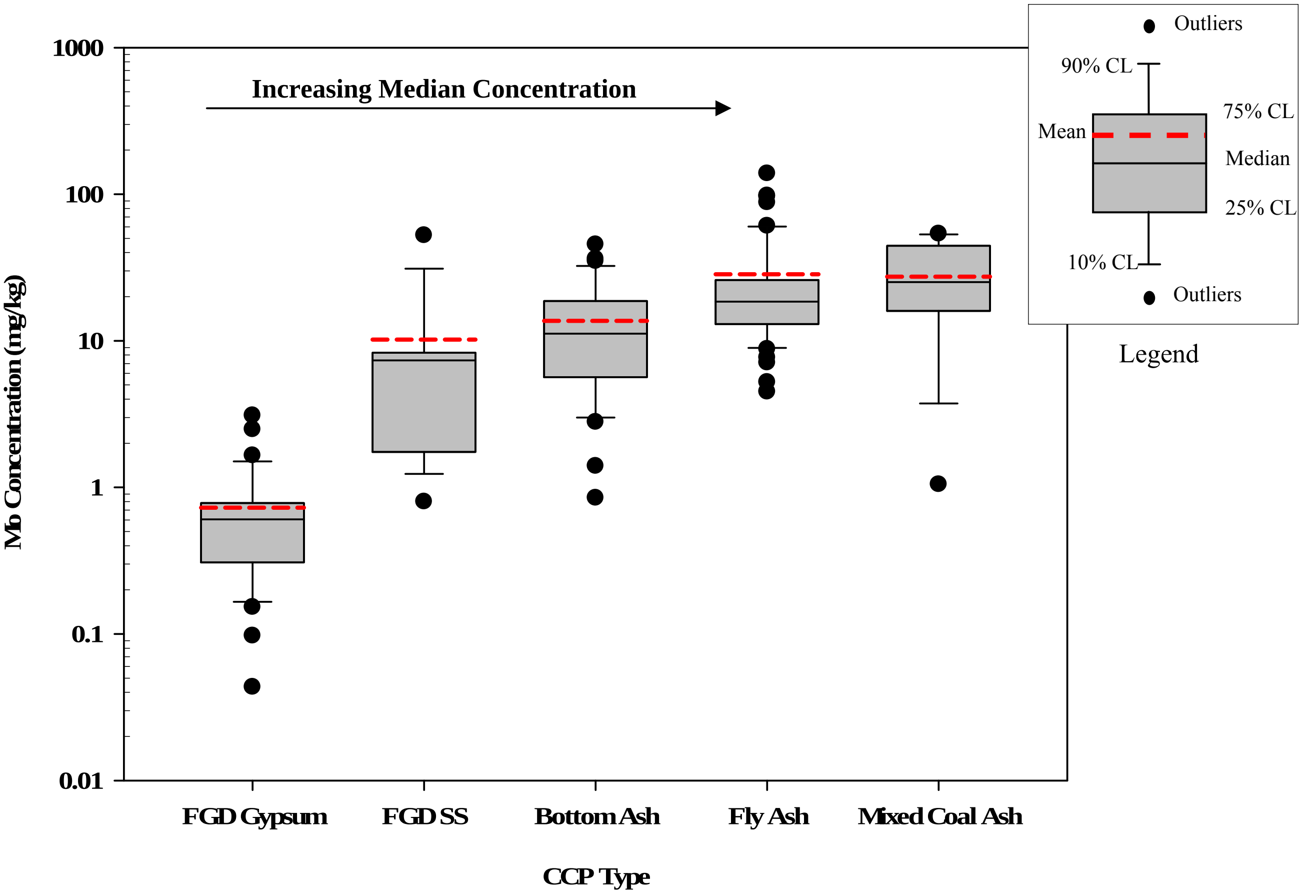
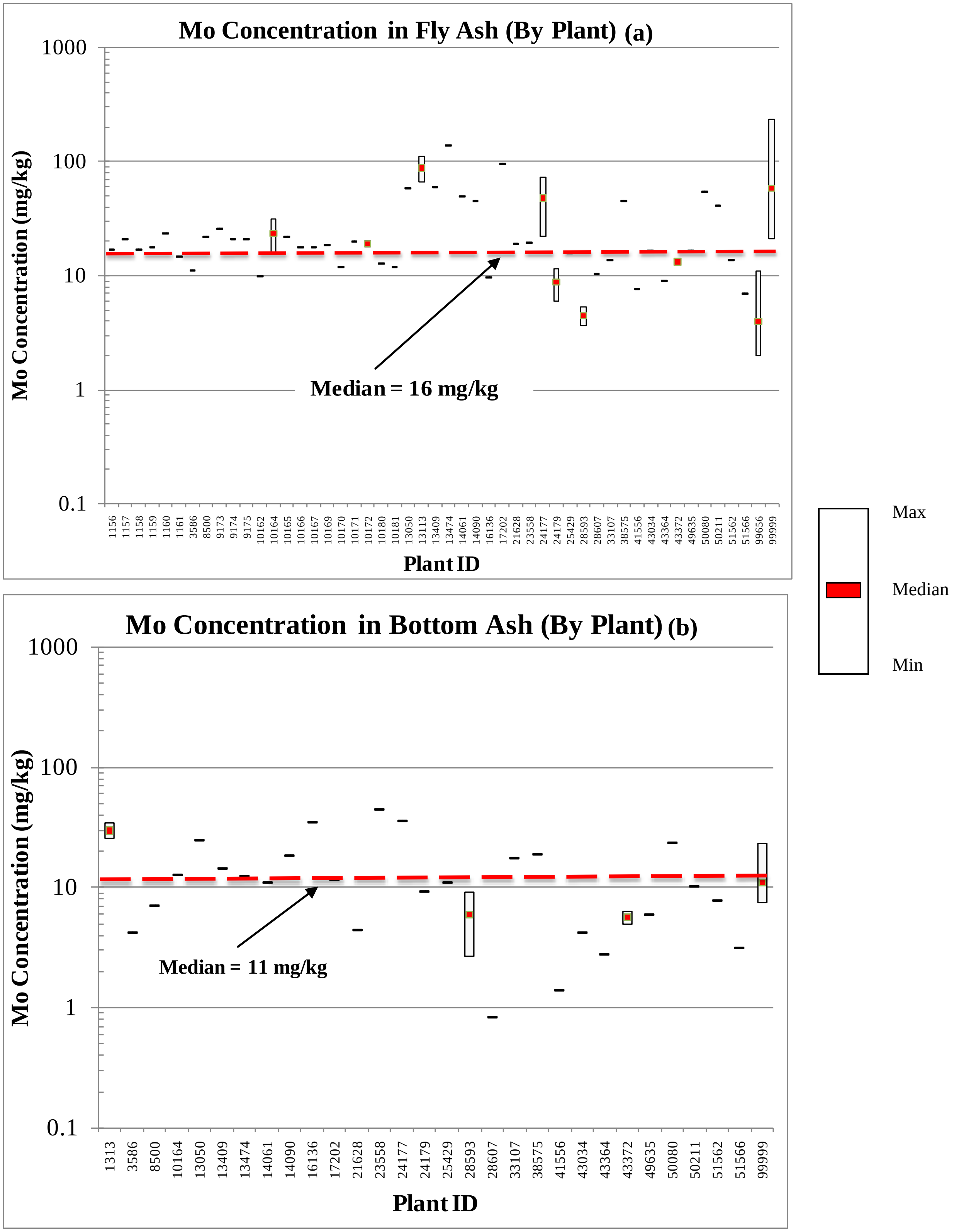


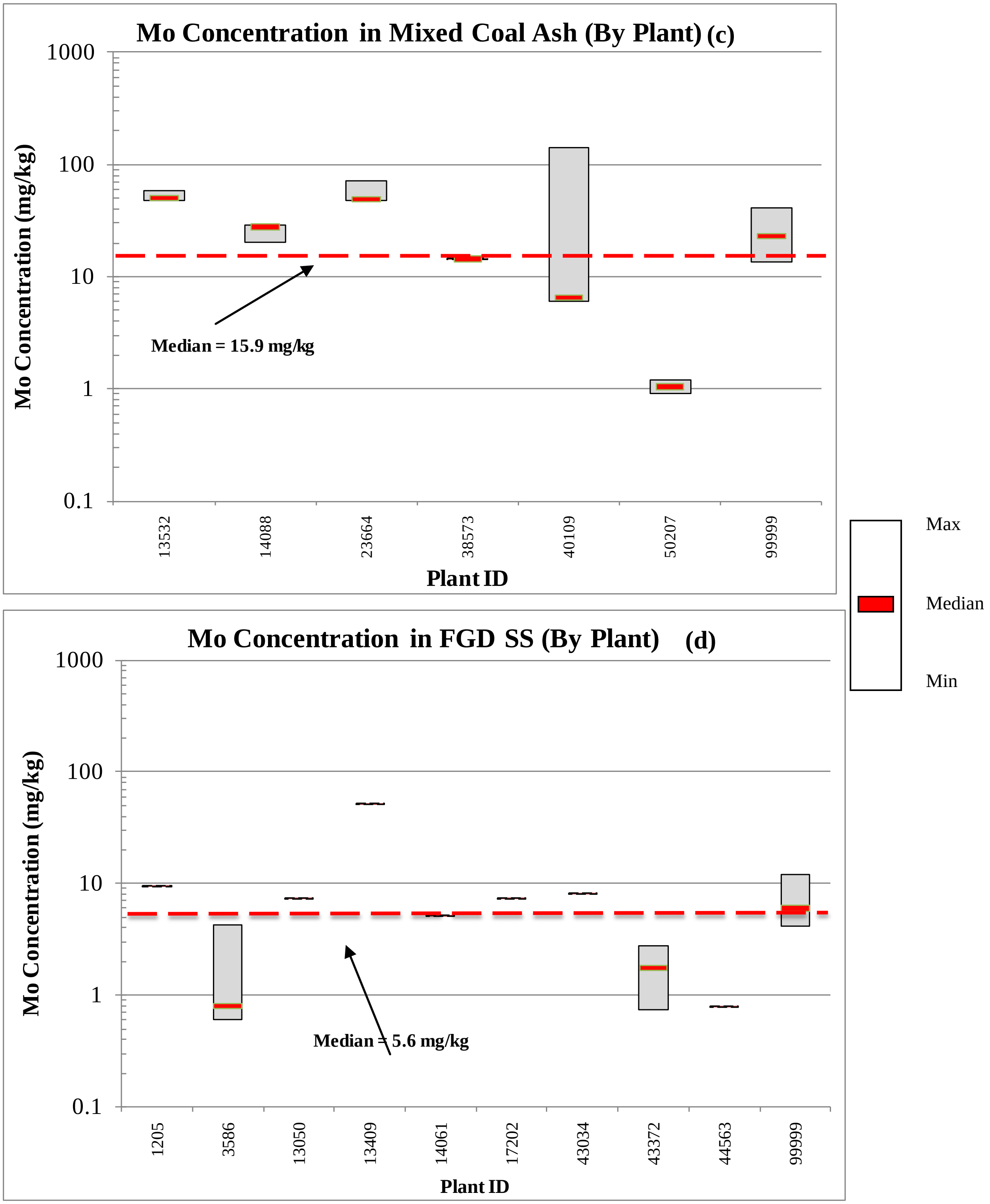
Figure 6-1
Molybdenum Concentrations in CCPs by CCP Type – Plant-Averaged Values

Notes: *See Table 6-1 for details.*
Data obtained from EPRI (2011a) dataset.



Mo Concentration in Fly Ash (By Plant) (a)

Mo Concentration in Bottom Ash (By Plant) (b)


Mo Concentration in Mixed Coal Ash (By Plant) (c)
1000
100
10
1
0.1
Mo Concentration (mg/kg)
Median = 15.9 mg/kg
13532
14088
23664
38573
40109
50207
99999
Plant ID
Max
Median
Min
Mo Concentration in FGD SS (By Plant) (d)
1000
100
10
1
0.1
Mo Concentration (mg/kg)
Median = 5.6 mg/kg
1205
3586
13050
13409
14061
17202
43034
43372
44563
99999
Plant ID

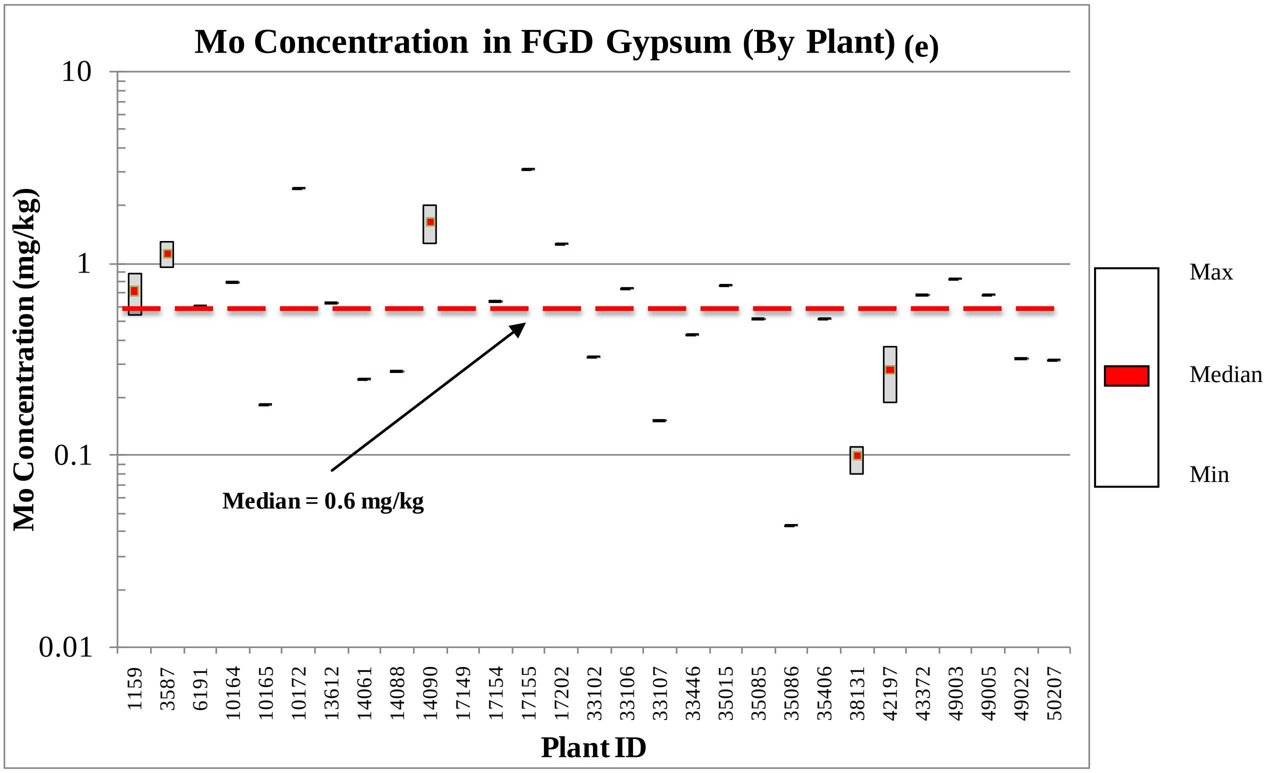


Figure 6-2 (a-e)
Molybdenum Concentrations in CCPs by Plant

The concentrations of Mo reported from the EPRI (2011a) dataset are generally consistent with other scientific literature. For example, Querol *et al*. (1995, 1996) determined the mean Mo concentrations in fly ash samples to be approximately 15 mg/kg. It was noted in the Querol *et al*. (1995, 1996) studies that Mo is more enriched in the smaller fly ash particles (< 2.5 µm) compared to larger size particles. In the Thorneloe *et al*. (2010) study, the range of Mo concentrations for 34 fly ash samples was 6.6-77 mg/kg, and the range of Mo concentrations in the FGD gypsum samples was 1.1-12 mg/kg. Querol *et al*. (1995) noted that Mo exhibited dual behavior during coal combustion: (1) volatilization during combustion; and (2) partial condensation of particles of high surface areas during flue gas and particulate removal (in the ESP and scrubbers), which would explain the observed Mo concentration in fly ash and FGD material. The variability within each CCP type can arise due to (1) variability in Mo concentration in the parent coal used; (2) variability due to differing combustion and emissions control technologies; and/or (3) the application of different analytical methods to measure Mo in CCPs. In addition, the waste management units typically accept CCPs generated from different coal types and separation technologies, potentially resulting in a concentration variance within an individual site.

6.1.2 Mode of Occurrence

Even though the characteristics and mineralogy of CCPs are well documented in literature, there is little information on the speciation and mode of occurrence of Mo in CCPs. The predominant mineral fractions in CCPs are oxides of aluminum (Al_2O_3), silicon (SiO_2), and iron (Fe_2O_3 or Fe_3O_4) (Hower *et al*., 2005). Other metal oxides, such as calcium and titanium oxide, also are present in coal ash and bottom ash in relatively minor quantities. Querol *et al*. (1996) noted that Mo has a greater affinity to iron oxides, calcium oxides, and calcium sulfate in CCPs. In their study, Querol *et al*. (1996) found that more than 40% of total Mo in fly ash was associated with readily leachable salts or oxides, such as metal sulfates and amorphous metal oxides. The remaining 60% of Mo was found to be associated with stable and/or recalcitrant minerals, such as crystalline iron oxides and alumino-silicate oxides. It was noted that, after combustion, Mo travels along with the flue gas and is captured with iron oxides, or it is sorbed onto calcium salts during the scrubbing process.

6.2 Molybdenum Concentrations in CCP Leachate

6.2.1 Factors that Affect Molybdenum Leaching Behavior in CCPs

6.2.1.1 pH

The pH of a CCP is determined primarily by the sulfur and calcium content of the parent coal and the type of coal combustion process that is used. The pH of CCPs affects the leachate pH, which in turn influences the mobility of metals, including Mo (Thorneloe *et al*., 2010; Carlson and Adriano, 1993; US EPA, 2009c). The effect of pH on the leaching behavior of Mo in CCPs is depicted in Figure 6-3, which is an illustrative leaching profile for fly ash at one plant as a function of pH (leaching profiles from other ashes included in US EPA, 2009c, show similar trends). This figure shows the general trend of higher Mo leaching in acidic and alkaline pH conditions and reduced leaching in the near neutral pH region. However, other factors besides pH (*e.g.*, total Mo concentration, the amount of calcium and sulfur present) influence both the shape of the leaching profile and the resulting leachate Mo concentrations.

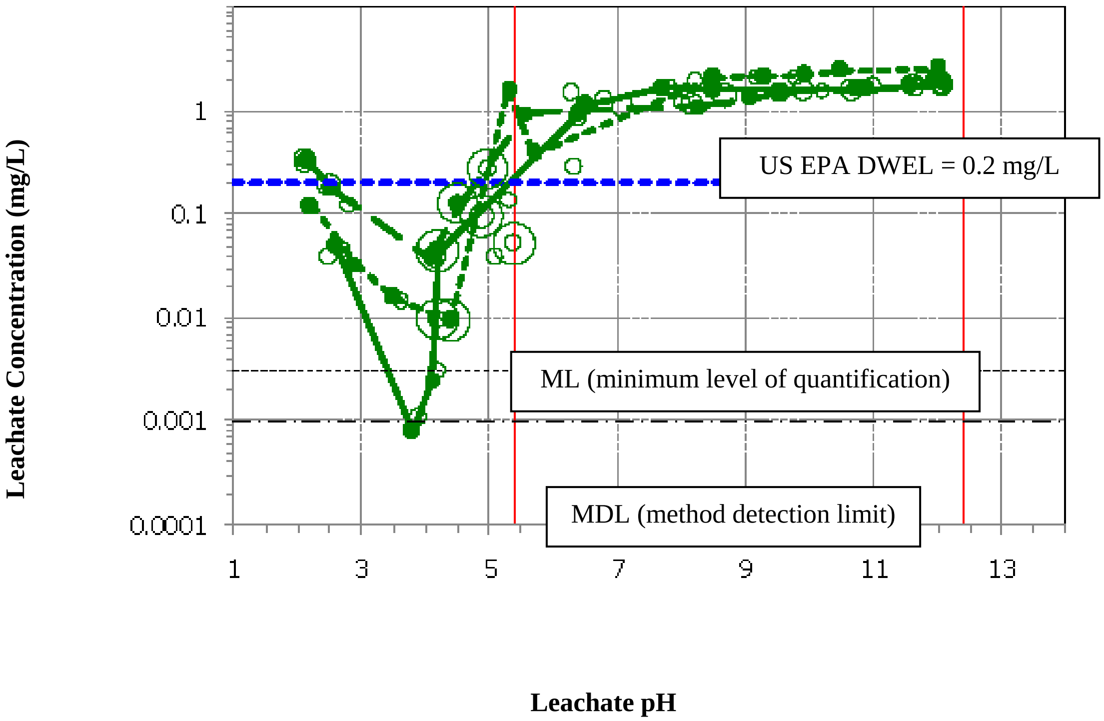


Figure 6-3
Illustrative Profile of Molybdenum Leaching from CCPs as a Function of pH

Note: Graph from US EPA, 2009c, "Facility E" leaching profile.

6.2.1.2 Mineralogical Composition

As stated previously, Mo has an affinity for iron oxides, calcium oxides, and calcium sulfate in CCPs (Querol *et al*., 1996). The relatively high leaching of Mo from coal fly ash, compared to other trace metals such as arsenic and selenium, in the Querol *et al*. (1996) study has been attributed to its association with soluble calcium salts.[5] Smichowski *et al*. (2008) noted that more than 40% of the total Mo in coal fly ash was associated with these soluble fractions. Tiruta-Barna *et al*. (2006) observed that Mo was associated predominantly with powellite, the dissolution of which controlled Mo leaching from coal ash.

6.2.1.3 CCP Weathering State

The weathering state of CCPs also influences Mo leaching. Dudas (1981) attributed higher Mo leaching from fresh, unweathered ash to its relatively higher fraction of soluble salts compared to weathered ash. With time, the amount of soluble salts decreases due to dissolution, resulting in decreased Mo leaching rates. EPRI (1987) and Al-Abed *et al*. (2008) reported similar findings on the effect of mineralogy on the leaching behavior of trace metals.

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[5] In general, calcium salts such as sulfates and carbonates in CCPs are readily soluble; leachable oxides such as amorphous iron oxides exhibit moderate solubility; and crystalline forms of iron, silicon, and aluminum oxides are less soluble (Querol *et al*., 1996).

6.2.2 Molybdenum Concentrations in CCP Leachate

This section presents data on Mo concentrations associated with CCP leachate. It is based on the EPRI (2011a) dataset, which includes Mo data from 306 field leachate samples collected from 34 plants, as well as 400 laboratory leachate samples from laboratory extraction tests performed on CCPs collected from 75 plants. Field samples were collected from surface impoundments and landfills from a variety of locations, including monitoring wells screened within the CCP zone, leachate collection systems, and surface impoundment outfalls from the various CCP disposal sites. Laboratory leachate samples were collected using different extraction methods to simulate variable leaching conditions. Data from scientific literature were used for comparison purposes.

Figure 6-4 shows the distribution of Mo concentrations in all samples from the EPRI (2011a) dataset, including all CCP types and all leachate types. The median concentration of Mo was 0.25 mg/L, while the mean value was approximately 1.1 mg/L.

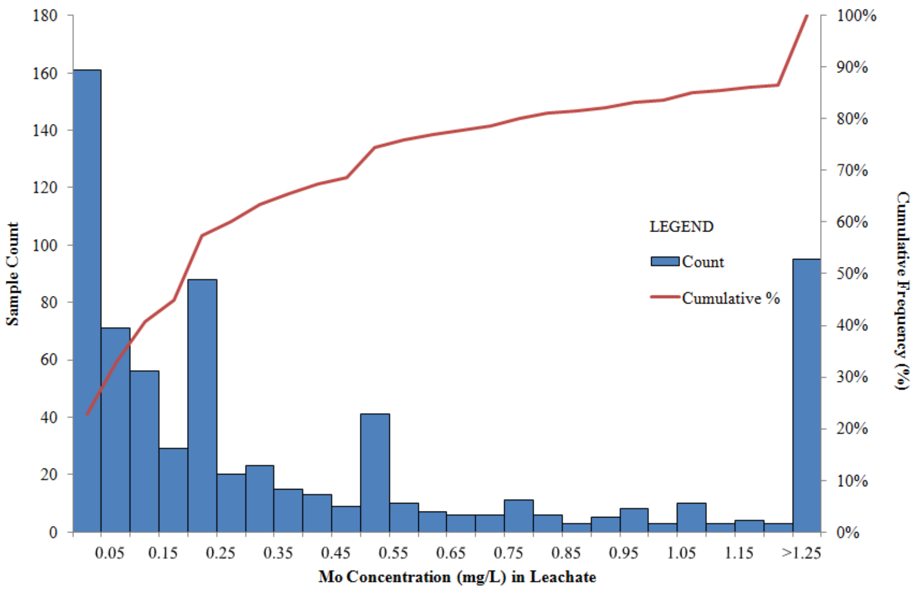

Figure 6-4
Molybdenum Concentration Distribution in Leachate – EPRI (2011a) Dataset

Notes: Includes all laboratory leachate and landfill and surface impoundment field leachate data from EPRI (2011a) dataset. The total number of discrete samples: n = 706 samples.

Non-detects were assumed to be half the detection limit.

Table 6-2 presents summary statistics of Mo leachate concentrations from the EPRI (2011a) dataset. These summary statistics are based on site-averaged data and classified by the CCP type reported in the dataset.[6] In general, the concentration of Mo in landfill field leachate samples was higher than in either laboratory leachate or surface impoundment field leachate samples. Among the different CCP types, the highest median and mean Mo concentrations were associated with leachate from fly ash and mixed coal ash (which is composed of fly ash with bottom ash) disposed of in landfills. FGD gypsum leachate had the lowest Mo concentrations.

Table 6-2
Molybdenum Concentration by CCP Type Site-Averaged Values[1]

CCP Type	Laboratory Leachate[2]					
	# of Plants	# of Sites	# of Discrete Samples	# of Non-Detects	Site-Averaged Data[3]	
					Mean (mg/L)	Median (mg/L)
Fly Ash	46	59	115	1	1.05	0.27
Bottom Ash	34	41	48	20	0.03	0.01
Mixed Coal Ash	13	19	160	71	0.42	0.28
FGD SS	10	13	27	14	0.52	0.11
FGD Gypsum	29	29	34	0	0.006	0.003
Fixated FGD	1	1	16	0	0.89	0.89

CCP Type	Field Leachate - Landfills[2]					
	# of Plants	# of Sites	# of Discrete Samples	# of Non-Detects	Site-Averaged Data[3]	
					Mean (mg/L)	Median (mg/L)
Fly Ash	8	9	32	0	6.85	4.48
Bottom Ash	-					
Mixed Coal Ash	5	8	47	6	2.11	1.03
FGD SS	-					
FGD Gypsum	-					
Fixated FGD	4	4	17	0	1.2	0.6

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[6] Most of the data within this chapter are described, evaluated, and presented on a "site-averaged basis." Because the number of samples collected from each disposal site varies, as does the number of disposal sites at each plant, an initial step was performed on each dataset – the arithmetic mean (average) Mo concentration for each CCP type at each "site" was calculated – so that the results are not biased high or low because of the sampling frequency at individual sites. Thus, for example, a descriptive statistic such as the "median site-averaged Mo concentration" means that half the sites had average concentrations exceeding this value, half below. Non-detect values were assumed to be half the reported detection limit.

Table 6-2
Molybdenum Concentration by CCP Type Site-Averaged Values[1] (continued)

CCP Type	Field Leachate - Surface Impoundments[2]					
	# of Plants	# of Sites	# of Discrete Samples	# of Non-Detects	Site-Averaged Data[3]	
					Mean (mg/L)	Median (mg/L)
Fly Ash	12	13	78	10	0.36	0.25
Bottom Ash	9	9	28	22	0.26	0.25
Mixed Coal Ash	16	18	85	20	0.62	0.15
FGD SS	5	6	19	5	5.33	0.22
FGD Gypsum	-					
Fixated FGD	-					

Notes: [1] Based on the EPRI (2011) dataset.

[2] Laboratory leachate includes results from multiple extraction methods; landfill leachate includes results from all landfill field leachate sample types; surface impoundment water includes results from all surface impoundment sample types.

[3] Calculated using the mean for each plant "sub-site" as a discrete value

6.2.1 Molybdenum Concentration in Coal Combustion Products Determined in Laboratory Extraction Tests

The EPRI (2011a) dataset contains results from studies in which CCPs were subjected to different extraction tests, including the Synthetic Precipitation Leaching Procedure (SPLP), centrifuging, and hot-water/nitric acid extracts. Chapter 7 provides further details on these methods. The extracts from the different methods are referred to as “laboratory leachate.”

Figure 6-5 show the Mo concentration in laboratory leachate from different CCP types based on the EPRI (2011a) dataset. The median site-averaged Mo concentrations ranged from 0.003-0.28 mg/L as follows: FGD gypsum < bottom ash < FGD SS < fly ash < mixed coal ash (fly ash mixed with bottom ash).

Overall, the Mo concentration in laboratory leachate from the EPRI (2011a) dataset is comparable to values reported in the scientific literature. For example, Roy *et al*. (1984) reported Mo concentration in Illinois Basin coal fly ash leachate extracted using the EP TOX and water extraction tests to be from 0.02-14.5 mg/L. The range reported in Thorneloe *et al*. (2010) was 0.0005-130 mg/L[7] for coal fly ash leachate and 0.0003-1.9 mg/L for FGD gypsum leachate samples. Mo leachate concentration from bituminous fly ash subjected to TCLP and groundwater leaching tests ranged from 0.5-2.5 mg/L (Hassett *et al*., 2005).

Figure 6-6 displays the laboratory leachate sampling results for fly ash from the various laboratory batch leaching tests, as well as a limited number of centrifuge extraction test data (centrifuge extraction of porewater from field cores) based on the EPRI (2011a) dataset. The

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[7] Thorneloe *et al*. (2010) reported that the highest Mo concentration observed was in a leaching test conducted at a liquid-solid ratio of 1 using deionized water, compared to the liquid-solid ratio of 20 (as mandated in the TCLP or SPLP tests). Leachate concentrations generally decrease with increasing liquid-solid ratios (*i.e.*, the maximum concentration is observed at low liquid-solid ratios) (US EPA, 2009c).

means of the site-averaged Mo concentration ranged from 0.44-10.78 mg/L, depending on the type of extraction test, while the medians ranged from 0.19-9.43 mg/L. The mean and median leachate values were almost an order of magnitude higher in the centrifuge extractions of porewater, compared to the SPLP and “Other Batch” extraction techniques.

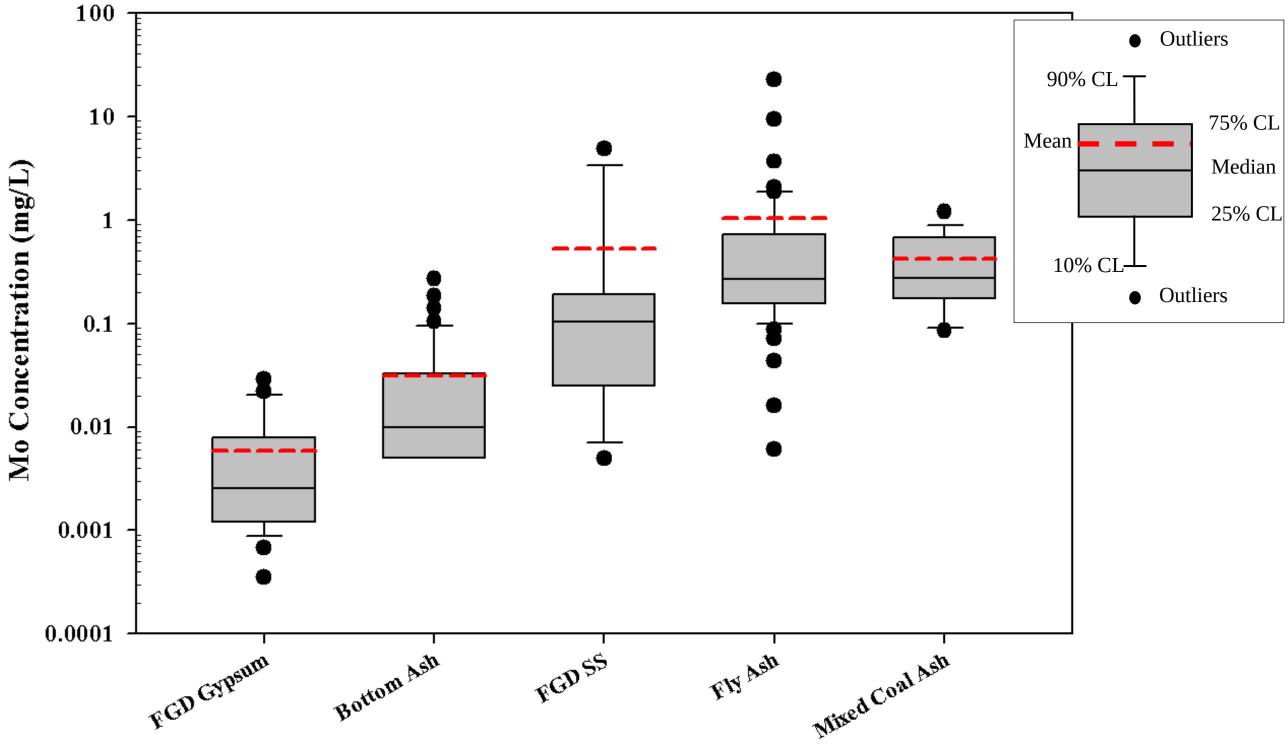

Figure 6-5
Molybdenum Concentrations in Laboratory Leachate

Notes: The total number of site-averaged values (n) are 1) Fly ash: n = 59; 2) bottom ash: n = 41; 3) FGD SS: n = 13; 4) Mixed coal ash: n = 19; and 5) FGD gypsum: n=29. Data from EPRI (2011a) dataset.

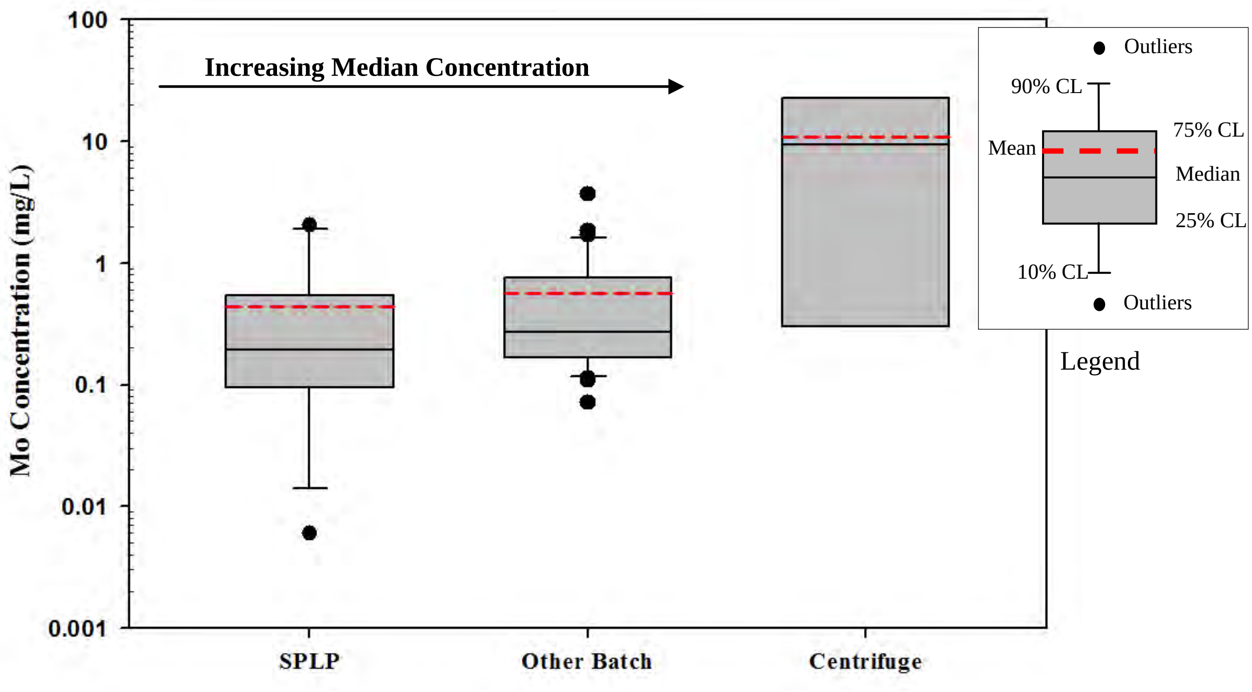

Figure 6-6
Molybdenum Concentrations in Fly Ash Leachate – Comparison of Laboratory Leachate Extraction Tests

Notes: The total number of site-averaged values (n) are 1) SPLP: n = 17; 2) Other Batch: n = 39; and 3) Centrifuge: n = 3. Data from EPRI (2011a) dataset.

6.2.2 Molybdenum Concentration in Landfill Leachate

Figure 6-7 presents the distribution of site-averaged Mo concentrations in landfill leachate from the EPRI (2011a) dataset. The site-averaged Mo concentration ranged from 0.1-25.4 mg/L for all CCP types. The mean and median of the site-averaged Mo concentration in the EPRI (2011a) dataset were highest in fly ash (6.85 and 4.48 mg/L, respectively; see Table 6-2). The highest site-averaged Mo concentration (25.4 mg/L) was observed for fly ash because of one sample that was almost 5-fold higher than the median value for fly ash. EPRI (2006a, p. 4-28) noted previously that leachate samples from this specific site had relatively high concentrations of elements (including Mo) because this power plant used a wider variety of fuel (*i.e.*, coal, petroleum coke, and tires) and high-temperature boilers.

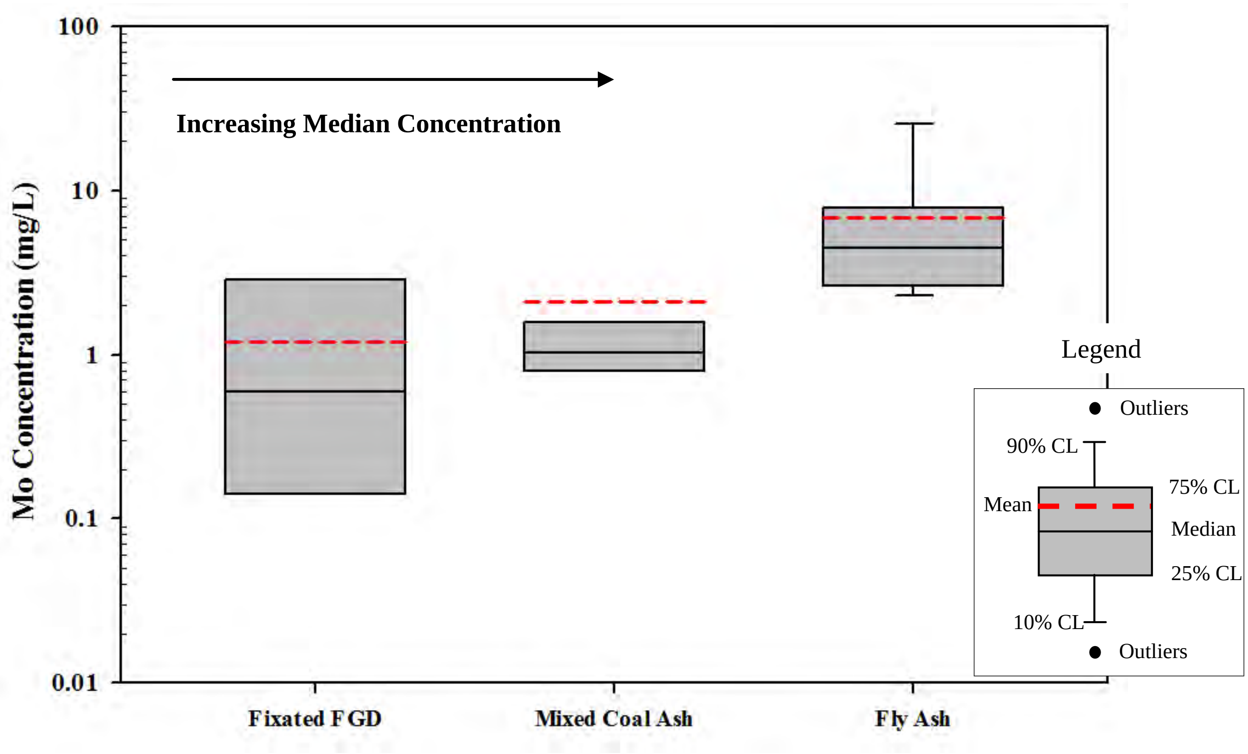

Figure 6-7
Molybdenum Concentrations in CCP Landfill Leachate

Notes: The total number of site-averaged values (n) are 1) fly ash: n = 9; 2) Mixed coal ash: n = 8; and 3) Fixated FGD: n = 4. Data from EPRI (2011a) dataset.

6.2.3 Molybdenum Concentration in Surface Impoundment Leachate

Figure 6-8 presents the distribution of site-averaged Mo concentrations in surface impoundment leachate from the EPRI (2011a) dataset. The mean and median concentrations were similar across all CCP types, except the mean FGD SS concentration, which appears to be skewed high because of one sample with a concentration of 60.8 mg/L (other samples collected from the same surface impoundment had much lower concentrations of Mo, < 1 mg/L). Overall, the Mo concentrations from surface impoundment samples were lower than from landfill leachate samples.

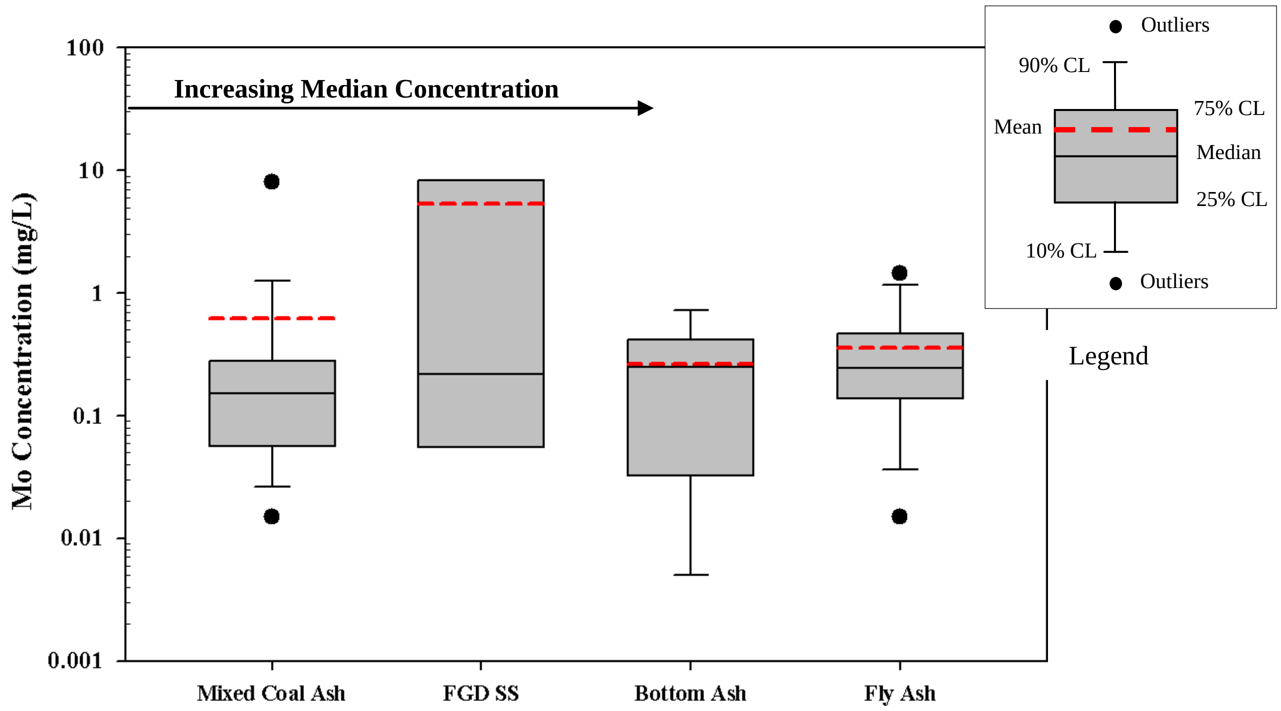

Figure 6-8
Molybdenum Concentrations in CCP Surface Impoundment Leachate

Notes: The total number of site-averaged values (n) are 1) fly ash: n = 13; 2) Bottom ash: n = 9; 3) Mixed coal ash: n = 18; and 4) FGD SS: n = 6. Data from EPRI (2011a) dataset.

6.3 Molybdenum Speciation in Coal Combustion Product Leachate

There is very little information on the speciation of Mo in CCP leachate. Mo is typically in the +6 oxidation state as an oxyanion (Morrison *et al*. 2006). At pH values > 5, Mo forms the water-soluble molybdate complex. Arai (2010) and LeGendre and Runnells (1975) noted that, under oxic environments and also high pH, Mo existed as molybdate oxyanions. Because CCP leachate in most landfills and surface impoundments has a pH > 5, it is more likely that the dominant form of Mo in leachate is molybdate.

7
ENVIRONMENTAL SAMPLING AND ANALYSIS

This chapter presents sample preparation and analysis methods for Mo in CCP-impacted matrices. Although the focus of this chapter is primarily aqueous matrices, such as CCP leachates and water, analysis methods for bulk CCP matrices are addressed briefly as well. Analyses of both solid and aqueous matrices are necessary to fully characterize potential exposure to Mo from environmental exposures.

7.1 Sample Preparation Methods for Coal Combustion Product Leachate

Laboratory leaching tests are widely used to determine the potential impact of metals and other constituents from CCPs on the environment (EPRI, 2005). Selection of an appropriate leaching method is highly dependent on overall data objectives, process/source of CCPs, intended management scenarios, and disposal conditions. Examples of leaching methods that have been investigated and implemented to characterize CCPs include those listed in Table 7-1.

Table 7-1
Examples of CCP Leaching Methods

Reference	Title	Comments
EPA SW846 Method 1311	Toxicity Characteristic Leaching Procedure (TCLP)	Simulates landfill disposal conditions.
EPA SW846 Method 1312	Synthetic Precipitation Leaching Procedure (SPLP)	Designed to evaluate the impact of contaminated soils on groundwater. Wastes can be sieved to < 2 mm to eliminate the particle size reduction step (see USGS, 2000).
ASTM D3987-85	Shake Extraction of Solid Waste with Water	Neutral extraction method.
18-hour leaching test	Modification of Shake Extraction of Solid Waste with Water	Extraction conditions are similar to ASTM D3987-85, but shaken for a duration of 18 hours.
30-day leaching test	Modification of Shake Extraction of Solid Waste with Water	Extraction conditions are similar to ASTM D3987-85, but shaken over 30 days.

Table 7-1
Examples of CCP Leaching Methods (continued)

Reference	Title	Comments
Ziemkiewicz, 2005; Ziemkiewicz and Knox, 2006	Mine Water Leaching Procedure (MWLP)	Evaluates behavior of ash in acidic conditions such as acid mine drainage. Involves a sequential extraction method that uses water from the intended application site. Accounts for chemical interactions between ions released from coal combustion by-products and those in the mine water. Continues leaching until all alkalinity is exhausted.
Hassett *et al*., 2005	Synthetic Groundwater Leaching Procedure (SGLP)	Simulates actual field conditions. Conditions similar to TCLP. Can incorporate Long Term Leaching (LTL) of 30- or 60-day equilibration times.
State of California, 2008	California Wet Extraction Test (WET)	Can be modified to use deionized water instead of citric acid (CWRCB, 2008).
ASTM D4874-95	Standard Test Method for Leaching Solid Material in a Column Apparatus	Flow-through column test involving aqueous leaching of a material in a dynamic partitioning manner.
ANSI/ANS-16.1-2003; R2008	Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure	Measures release from waste forms as a result of leaching in demineralized water for 5 days; similar methods have been used to evaluate leaching from CCPs reused to make cement (US EPA, 2008).
Leaching Environmental Assessment Framework (LEAF) (http://vanderbilt.edu/leaching/leaf/)	LEAF Method 1313 – pH Dependence	Evaluates chemical leaching as a function of pH.
	LEAF Method 1314 – Percolation Column	Assesses percolation through loosely packed material.
	LEAF Method 1315 – Mass Transfer Rates	Assesses the flux and cumulative chemical leaching as a function of leaching time.
	LEAF Method 1316 – Batch Liquid-Solid Partitioning	Evaluates leaching as a function of liquid-solid partitioning.

Some state agencies have expressed concern regarding the wide variety of leaching procedures available, the lack of correlation between these methods and/or bulk sample analyses, and the lack of data comparability (US EPA, 2009c). For example, it is possible that standard methods such as TCLP and SPLP will not be appropriate for determining leaching from CCPs *in situ* or under actual waste management conditions because these methods use standard leaching solutions and do not necessarily predict interactions between the solid waste and components of a specific mine water (Ziemkiewicz and Knox, 2006). A framework for more appropriate and reliable leaching methods (Leaching Environmental Assessment Framework, or LEAF) has been under examination by Vanderbilt University and US EPA so that CCP data comparability eventually may be improved; the methods evaluated by US EPA focus on leaching as a function of pH and liquid-to-solid (LS) ratio (US EPA, 2009c, 2010c). Additional testing methods following this framework (listed in Table 7-1) have been developed and currently are under review and validation for inclusion in US EPA's SW846 test method compendium.

7.2 Laboratory Methods for Analyzing Molybdenum

Numerous standard methods (Table 7-2) are available for analyzing Mo in leachates and CCP-impacted matrices. The majority of the methods involve inductively coupled plasma (ICP) analyses and are multi-element, allowing for characterization of multiple metals at once. In contrast, some of the flame and graphite furnace atomic absorption (AA) methods are specific to Mo. Detection limits range from 0.30-100 µg/L in aqueous matrices and 0.004-8 mg/kg in solid matrices. In general, the inductively coupled plasma/mass spectrometry (ICP-MS) and AA methods offer more sensitive detection limits than the ICP-atomic emission spectroscopy (ICP-AES) methods.

Table 7-2
Methods for Analysis of Molybdenum

Source	Method Number	Method Name	Approximate Detection Level
Aqueous Matrices (Water and Leachates)			**µg/L**
US EPA Drinking Water Methods	200.7	Metals in Water by ICP-AES	4
	200.8	Metals in Water by ICP-MS	0.3
	246.1	Molybdenum by Flame AA, Direct Aspiration	100
	246.2	Molybdenum by Graphite Furnace AA	1
Standard Methods for the Examination of Water and Wastewater	3113B	Metals in Water by GFAA	1
	3120B (total)	Metals (Total Recoverable) in Water by ICP	4
	3125	Metals in Water by ICP-MS	8
US EPA SW846	6010C	Trace Elements in Solution by ICP-AES	5.3
	6020A	ICP-MS	8
	6800	Elemental and Speciated Isotope Dilution Mass Spectroscopy	8
	7081	Graphite Furnace Atomic Absorption Spectrophotometry	1
AOAC International	990.08	Metals in Solid Wastes by ICP	8

Table 7-2
Methods for Analysis of Molybdenum (continued)

Source	Method Number	Method Name	Approximate Detection Level
Aqueous Matrices (Water and Leachates)			**µg/L**
ASTM	D1976	Elements in Water by ICP-AES	8
	D5673	Elements in Water by ICP-MS	2.8
USGS-NWQL	I-1472-87	Metals in Water by ICP	10
	I-1492-96	Molybdenum in Water by Graphite Furnace Atomic Absorption Spectrophotometry, Filtered	0.9
	I-3492-96	Molybdenum in Water by Graphite Furnace Atomic Absorption Spectrophotometry, Unfiltered	0.9
	I-4471-97	Metals in Water by Inductively Coupled Plasma/Optical Emission Spectrometry, Whole-Water Recoverable	34
	I-4472-97	Metals in Water by Inductively Coupled Plasma/Mass Spectrometer, Whole-Water Recoverable	0.4
Solid/Bulk CCP Matrices			**mg/kg**
US EPA Drinking Water Methods	200.2	Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements	Not applicable
US EPA SW846	3050B	Acid Digestion of Sediments, Sludges, and Soils (sample preparation method)	Not applicable
	3052	Microwave Assisted Acid Digestion of Siliceous and Organically Based Matrices	Not applicable
	6010C	Trace Elements in Solution by ICP-AES	5
	6020A	ICP-MS	0.004
	6200	Field Portable X-Ray Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment	20
	6800	Elemental and Speciated Isotope Dilution Mass Spectroscopy	8

Notes: *AA = Atomic Absorption Spectroscopy*
AOAC = Association of Official Agricultural Chemists
ASTM = American Society for Testing and Materials
GFAA = Graphite Furnace Atomic Absorption Spectroscopy
ICP = Inductively Coupled Plasma
ICP-AES = Inductively Coupled Plasma-Atomic Emission Spectroscopy
ICP-MS = Inductively Coupled Plasma-Mass Spectrometry
USGS-NWQL = United States Geological Survey National Water Quality Laboratory

7.3 Analytical Interferences

It is possible that, due to high metal content, matrix interferences may occur, resulting in problems with the metal's quantitation and accuracy of results. For example, high concentrations of other metals (*e.g.*, aluminum and iron) may cause spectral interferences for Mo during ICP-AES analyses; these interferences occur when wavelengths from other analytes overlap with or are close to the wavelength of the analyte of interest, resulting in false positives. In other cases, concentrations of interfering analytes may be so high that they actually suppress analyte signals, causing false negatives. Physical interferences from high solids or acid content also may occur, increasing sample viscosity and affecting absorption, nebulization, and sample transport. Also, Mo can act as a spectral interferent for other analytes (*e.g.*, vanadium) in ICP-AES analyses.

There are several potential sources of interference during ICP-MS analyses. For example, isobaric elemental interferences may occur due to isotopes of different elements that form singly or doubly charged ions of the same nominal mass-to-charge ratio. Physical interferences (high solids, high viscosity) may hinder transport of the sample into the plasma. In addition, signals from relatively abundant isotopes can cause loss of resolution and poorer quantitation. Isobaric polyatomic ion interferences are caused by ions consisting of more than one atom with the same nominal charge-to-mass ratio of the isotope of interest. Finally, memory interferences (carry-over) of isotopes can occur from previous sample runs. It should be noted that, at concentrations of 1 mg/L and above, Mo can cause molecular ion interferences and potential false positives for cadmium in ICP-MS analyses (USGS, 1998b). Also, Mo is used as a labeled standard in US EPA Method 6020A; this should be taken into consideration when designing any analysis program involving this method.

In general, the various published methods provide information and guidance regarding interferences and how to correct them during sample analysis. For example, background correction techniques (such as interelement corrections in ICP, Zeeman background correction in graphite furnace AA) can be implemented, while the use of internal standards generally alleviates interferences encountered during ICP-MS. Sulfate can interfere in the determination of Mo during graphite furnace AA analysis, but matrix modifiers such as magnesium nitrate and ammonium can minimize this interference. Mo also can form carbides, resulting in memory-effect (carry-over) interference; these can be eliminated by routine intermittent blank-sample analysis, a multistep high-temperature cleanout program, and the use of pyrolytically coated graphite tubes (USGS, 1997).

7.4 Molybdenum Speciation Analysis

At present, there appears to be little information available regarding Mo speciation in CCP matrices, and no standard methods were identified for Mo speciation analysis. This is most certainly an area requiring further research and development, specifically with regard to appropriate preservation methods, holding times, and factors affecting the stability of the species. The intended use and data objectives (*e.g.*, toxicity evaluations) of speciation data are critical to considering the need for speciation analysis or method development.

8

TREATMENT AND REMEDIATION

This chapter discusses remediation technologies for Mo at CCP disposal sites. The most viable remediation technologies for the treatment of aqueous Mo are adsorption and chemical precipitation, while biological treatment and membrane filtration are promising, but not yet proven, remediation techniques. Information sources used for this chapter include earlier EPRI reports on related topics (*e.g.*, EPRI (2006b)), scientific literature regarding metals remediation, and case studies for Mo-impacted sites. Mo is most often present as a co-contaminant of secondary concern at these sites (*i.e.*, it is not the primary remedy driver) and is often associated with other metals, including uranium.

At CCP disposal sites, impacted groundwater can be extracted and treated *ex situ* using conventional "pump-and-treat" (P&T) methods or *in situ* using permeable reactive barriers (PRBs) and subsurface injection. A PRB is used to hydraulically intercept and react with impacted groundwater that "passively" flows through some kind of reactive media using natural hydraulic gradients. As described in detail in EPRI (2006b), PRBs can be, and have been, used effectively to remediate metals such as Mo via precipitation and adsorption, often at lower estimated cost than P&T technology, although issues such as precipitate fouling could affect long-term performance. For example, Morrison *et al*. (2006) investigated the remediation of groundwater contaminated with uranium and Mo using a zerovalent iron PRB. Mo concentration in groundwater were reduced from 4.8 mg/L to < 0.1 mg/L over one year of operation, which was attributed to its precipitation or adsorption on iron oxides. McGregor *et al*. (2002) investigated the use of PRB to treat groundwater impacted by CCP leachate. It was noted in their study that PRB was successful in remediating Mo from groundwater, with removal efficiencies ranging from 80-99% (*i.e.*, Mo concentration reduced from almost 1 mg/L to < 0.07 mg/L). The data also indicated the removal of other trace elements, such as arsenic, selenium, and chromium, from groundwater.

Some of the key properties of Mo discussed in this report that are relevant to its treatment and remediation include:

- Mo has relatively low K_d values, ranging from 0.6-501 L/kg, which indicate that it has relatively high groundwater mobility. Other metals associated with CCP disposal sites that have similarly high mobility include boron, chromium, lithium, selenium, and strontium (EPRI, 2006b, Table 2-3).
- Mo typically exists as the negatively charged molybdate ion (MoO_4^{2-}) with pH-dependent behavior and sorption characteristics generally similar to those of other oxyanion-forming metals such as arsenic and selenium.
- Mo adsorption is highly pH-dependent. Peak adsorption for most sorbents (except maghemite nanoparticles) is at pH < 5 and limited adsorption occurs at pH > 8. In alkaline conditions, Mo behaves conservatively and its dissolved concentration is controlled by precipitation, not

adsorption, reactions. When present in sufficient concentrations, lead, then calcium, control Mo precipitation, forming wulfenite and powellite, respectively. For comparison, CCP leachates commonly have neutral to alkaline pH and are typically moderately to strongly oxidizing.

- Mo is typically present in CCP leachate at concentrations of about 0.25-1.1 mg/L, but concentrations can range up to 25 mg/L or more. US EPA has not established an MCL or MCLG for Mo, but the US EPA DWEL and tap water RSL of 0.2 mg/L and 0.18 mg/L, respectively, are non-enforceable federal regulatory screening criteria. Based on the EPRI (2011a) dataset, the site-average leachate Mo concentration exceeded 0.18 mg/L at about two-thirds of sites sampled.

The rest of this chapter provides an overview of individual remediation technologies for Mo.

8.1 Adsorption Techniques

Adsorption is a surface phenomenon by which constituents, such as dissolved Mo, become associated with solids. Adsorption can permanently or temporarily bind constituents and, as described in Chapter 5, can be quite geochemically complex. Adsorption techniques can be effective in treating Mo in water associated with CCPs, but most sorbents are not effective in alkaline conditions (except for maghemite nanoparticles, which studies indicate are effective even at high pH).

Adsorption techniques can be applied *ex situ* via groundwater extraction then treatment, or *in situ* via PRBs. Table 8-1 provides a summary of studies that have been performed on the use of sorbents, including iron and aluminum oxides, for Mo removal. The rest of this sub-section provides further details on these sorbents based on the studies referenced in Table 8-1.

Iron and Aluminum Oxides – As mentioned previously, studies of Mo sorption on iron and aluminum oxides and soil minerals have noted maximum Mo sorption (near complete removal) at the pH range 4-5. Mo sorption decreases with increasing pH > 5 (Goldberg *et al*., 2008; Arai, 2010).

The main mechanism of Mo sorption to oxides of iron and aluminum is through the formation of stable surface complexes (Goldberg *et al*., 2008). Xu *et al*. (2006) noted that the adsorption of Mo on the iron oxides pyrite and goethite is dependent on the Mo species present. Tetrathiomolybdate (MoS_4^{2-}) had greater sorption to goethite and pyrite than molybdate. Adsorption efficiency also was dependent on the presence and/or absence of competing ions, such as phosphate and sulfate. For example, the sorption of molybdate ions to goethite and pyrite decreased almost 30% in the presence of phosphate, while the sorption of tetrathiomolybdate decreased 15-20%. The presence of other competing ions, such as sulfate and silicate, did not have a significant effect on Mo sorption to goethite and pyrite.

Table 8-1
Summary of Sorbents for Molybdenum Remediation

Sorbent	Mo Removal	Factors Affecting Removal	Mechanism	Reference
Iron and aluminum oxides (*e.g.*, goethite, Al_2O_3, and pyrite, FeS_2)	Almost 100% removal observed at pH < 5	Presence of phosphate	Formation of surface complexes	Goldberg *et al*., 2008; Arai, 2010; Xu *et al*., 2006
Maghemite (Fe_2O_3) nanoparticles	Complete Mo removal across pH; fast sorption kinetics; sorption decreased with increasing pH	Slight decrease in Mo removal in the presence of sulfate ions	Surface complexation and electrostatic attraction	Afkhami and Norooz-Asl, 2009
Activated carbon	Maximum Mo sorption in acidic pH; significant decrease in removal with increasing pH	N/A	Electrostatic attraction	Afkhami and Conway, 2002
Hydrocalumite and ettringite	Strong Mo sorption at alkaline pH conditions; near complete removal	N/A	Ion substitution	Zhang and Reardon, 2003
Chitin	80-100% removal from mining effluent	Sorption decreases at alkaline pH	Electrostatic attraction	Moret and Rubio, 2003
Surface-modified zeolite	Only 30% Mo removal from 0.8-0.6 mg/L	N/A	N/A	Neupane and Donahoe, 2009

Note: N/A = not available.

***Maghemite Nanoparticles* –** Maghemite nanoparticles have higher adsorption capacity due to their highly active surface sites and faster sorption kinetics than their macro-sized counterparts. They are also effective over a relatively wide pH range (2-10), unlike other Mo sorbents.

Afkhami and Norooz-Asl (2009) studied the removal of Mo using maghemite (γ-Fe_2O_3) nanoparticles. Mo removal was consistently high (> 75 %) over a wide pH range (2-10). The Mo concentration in the maghemite-treated water reduced from 100 mg/L to < 3 mg/L within a reaction time of 15 minutes. Unlike goethite and other iron oxides, maximum Mo sorption (*i.e.*, near complete removal) was observed at near neutral pH. A slight decrease in Mo sorption was observed at pH > 9. Afkhami and Norooz-Asl (2009) attributed this high Mo sorption to 1) electrostatic attraction of negatively charged molybdate ions to the positively charged maghemite surface at acidic pH; and 2) formation of iron-molybdate complexes at alkaline pH. Furthermore, it was observed in this study that the presence of common anions such as nitrate, chlorides, and sulfate had an insignificant effect on Mo adsorption.

***Activated Carbon* –** Activated carbon has been used to remove Mo from aqueous solutions. Afkhami and Conway (2002) used a high surface area carbon cloth to remove molybdate from aqueous solutions. Similar to iron oxides, maximum Mo sorption was observed in acidic pH conditions, and the adsorption of Mo in near neutral pH was very low. Afkhami and Conway (2002) noted that, at extreme acidic conditions (pH 1.2), sorption of Mo decreased due to the formation of other condensed molybdates (*i.e.*, molybdates with octahedral structures).

Hydrocalumite and Ettringite – Zhang and Reardon (2003) studied the substitution of Mo on hydrocalumite and ettringite, as a mechanism of Mo removal. During the leaching of fly ash in alkaline environments, hydrocalumite (Ca2Al(OH)6.5Cl0.53(H2O)) and ettringite (Ca6Al2(SO4)3(OH)1226(H2O)) are formed as secondary precipitates, which can immobilize Mo via substitution/co-precipitation reactions. The authors observed that hydrocalumite and ettringite significantly removed dissolved Mo under alkaline pH conditions, and the mechanism involved was OH- and SO42- ion substitution. The Mo concentration was reduced to < 0.1 mg/L in treated water (from ~ 10 mg/L).

Chitin – Chitin is obtained from shells of crustaceans, such as shrimp and oysters. It can be described as cellulose with one hydroxyl group on each monomer substituted with an acetyl amine group, and it is rich in calcium carbonate and proteins. Chitin has been used successfully to treat Mo from aqueous solutions (Moret and Rubio, 2003). Moret and Rubio (2003) observed complete Mo removal from both mining effluents and synthetic aqueous solutions, attributing it to electrostatic attractions. Like other adsorbents, higher Mo sorption was observed in acidic pH. However, Mo desorption occurred at alkaline pH (pH 12), which would be useful in regenerating the adsorbent.

Zeolite – Mo also adsorbs to sorbents such as surface-modified zeolite (Neupane and Donahoe, 2009; EPRI, 2011b). Zhang and Reardon (2003) studied the adsorption of Mo from fly ash leachates and observed that up to 30% of Mo in the acidic and alkaline fly ash leachates was removed by zeolite treatment.

8.2 Chemical Precipitation

Chemical precipitation techniques, used widely to treat wastewater from coal-fired power plants, can be used to remediate Mo. In a chemical precipitation wastewater treatment system, chemicals are added to wastewater to alter the physical state of dissolved and suspended solids to facilitate settling and removal of the solids (US EPA, 2009a). Some of the common chemicals used as precipitating agents include lime (for hydroxide precipitation), ferrous or ferric chloride (iron co-precipitation), and sulfide salts (*e.g.*, sodium sulfide). Ferric chloride and a novel process of “electrocoagulation” have been used to chemically precipitate Mo from water, as described further below. Chemical precipitation is performed *ex situ* via groundwater extraction then treatment or *in situ* by injection of calcium polysulfide to precipitate soluble metals, for example.

LeGendre and Runnells (1975) observed a strong pH dependence on Mo removal using ferric chloride. Maximum Mo removal (almost 80%) was observed at acidic pH, and Mo removal decreased to 50-60% in the alkaline pH range. The ratio of Fe:Mo required for near-complete Mo removal (from an initial Mo concentration of 1.1-11.1 mg/L) was observed to be 10-100 (on a molar basis). US EPA data (2009c) obtained from four power plants that use chemical precipitation techniques for treating FGD wastewater showed a 50% decrease in Mo concentration with the use of lime and ferric chloride as precipitating agents.

Chellam and Clifford (2002) investigated the removal of Mo from leachate generated from the surface disposal of uranium mine tailings, using ferric chloride as a coagulant. Mo removal was greater at acidic pH (pH 4) than at alkaline pH. The increased Mo removal at acidic pH was attributed to the formation of inner-sphere complexes with iron, similar to those observed with goethite. Decreased removal at alkaline conditions was a result of electrostatic repulsion between the negatively charged Mo ions and negatively charged $Fe(OH)_4^-$ molecules (formed during the coagulation process). Also, increased removal efficiency by increasing iron concentration was noted.

Mills (2000) used a relatively new electrocoagulation process to remove Mo from leachate generated at mining sites. In this process, a series of electrolytic cells containing iron anodes and stainless steel cathodes were used. Application of direct current (DC) results in the generation of iron cations (*i.e.*, Fe^{3+}) at the anode and hydroxide ions (OH^-) at the cathode; the resulting iron hydroxide acts as a precipitating agent. The advantage of this process, as noted by Mills (2000), was the continuous generation of iron hydroxides. Almost 100% Mo removal, from 10 mg/L influent concentration to non-detect effluent concentration, was observed using this method. This technique also was effective in treating other trace elements such as arsenic and selenium. The presence of high concentrations of phosphate and sulfate had an insignificant effect on Mo removal efficiencies.

8.3 Biological Treatment

Bioremediation can be an effective technology for treating trace metals that are similar to Mo, such as arsenic and selenium. Microbial reduction of aqueous Mo could potentially immobilize Mo via the formation of insoluble Mo sulfides; however, very few studies have investigated this microbially mediated reduction, so the viability of this remediation technique at CCP disposal sites has not been demonstrated yet. These studies are described briefly below.

Kauffman *et al*. (1986) investigated the use of microbial treatment of uranium-impacted mine water that also contained Mo. Soils rich in sulfate-reducing bacteria were used in anaerobic reactors to treat uranium and Mo. The decrease in Mo concentration, from almost 1 mg/L to < 0.05 mg/L, was a result of the microbially mediated reduction of Mo to insoluble Mo sulfide (molybdenite).

In his review article, Lloyd (2003) noted that several sulfate-reducing bacteria (*e.g.*, *D. desulfuricans*, *T. ferrooxidans*) were able to immobilize Mo (VI) from solution at a very high efficiency.

Nelson *et al*. (2003) investigated the *in situ* anaerobic biological immobilization of Mo in groundwater using soil columns. The soils were rich in sulfate-reducing bacteria and the system was anoxic; *i.e.*, the redox potential was negative. The reduction of sulfate to sulfide, indicated by the generation of H_2S gas, resulted in reduction of Mo (VI) in the groundwater. The study observed complete Mo reduction (from an initial Mo concentration of up to 15 mg/L) over a 30-day period. Post-treatment flush tests to assess stability of the insoluble Mo sulfides showed minor remobilization of Mo.

Sivula *et al*. (2007) investigated the treatment of leachate generated from municipal solid waste incinerated (MSWI) bottom ash using anaerobic biological treatment. Leachates were treated in bioreactors containing digested sludge obtained from a municipal wastewater treatment plant

(WWTP). Sivula *et al*. (2007) noted almost 90% Mo reduction over a half-year period that was attributed to the formation of insoluble Mo sulfides and the complexation of Mo with organic matter. It was, however, observed that increasing the amount of organic matter increased formation of Mo-organic matter complexes. As a result, free Mo ions were not available for the microbial reduction process. The precipitation of calcium also inhibited the reduction process.

8.4 Membrane Filtration

Reverse osmosis (RO) is a physical separation process in which pretreated source water is delivered at moderate pressures against a semi-permeable membrane. The membrane rejects most solute ions and molecules while allowing water of very low mineral content to pass through. Nanofiltration is similar to RO in its mechanism, except that low pressures are applied. Chellam *et al*. (2002) found the efficacy of nanofiltration and RO techniques to achieve near complete removal of Mo, even from highly alkaline solutions (pH 10). Because anion repulsion is the predominant removal mechanism by the negatively charged membranes, greater ion rejection (or removal) was observed.

9

SUMMARY

- Mo is a naturally occurring transition metal that can be found in the environment in several different valence states; the most common valence state for naturally occurring Mo minerals is Mo (+4). In water, the Mo (+6) valence state (molybdate ion, MoO_4^{2-}) dominates Mo aqueous speciation except under low pH (< 4) and anoxic conditions.
- Mo is the least abundant of the biologically essential trace elements in soil. Worldwide concentrations of Mo in soils vary from about 0.1-10 mg/kg, with an average concentration of about 1-2 mg/kg. Overall, measured Mo concentrations in water appear to be highly variable, with a large percentage of surface and drinking water sources having levels below detection limits (about 5 µg/L or less). Averages for detectable levels of Mo in surface water have been reported to be below 100 µg/L.
- Mo is an essential nutrient that is necessary to normal biological function. The National Academy of Sciences has developed recommended dietary allowances for Mo ranging from 2-50 µg/day, depending on the age group.
- While Mo at low levels is necessary for optimal health, Mo at high levels can be associated with adverse effects via oral exposure. The most common health effects observed are increased uric acid production and gout. Based on these health endpoints and accounting for a margin of safety, US EPA has established an RfD for Mo of 0.005 mg/kg-day.
- According to US EPA, the information to evaluate the carcinogenic potential for Mo in humans or animals is inadequate. Also, Mo deficiency has been suggested to be associated with an increase in cancer incidence.
- Molybdate, which is an essential nutrient for microorganisms, plants, and animals, is the Mo species that plants and animals take up most readily from soil and water. Several different environmental factors (*e.g.*, pH, soil OC, aluminum and iron oxide, and soil sulfate) influence the extent of Mo uptake, bioaccumulation, and toxicity.
- Ruminants (*e.g.*, cows) are particularly sensitive to Mo toxicity and can develop a condition called molybdenosis, which is characterized by Mo-induced copper deficiency.
- Similar to other oxyanions such as Cr (VI) and Se (VI), molybdate is relatively mobile in groundwater. K_d values for molybdate range from 0.6-501 L/kg.
- Mo adsorption on both minerals and organic matter is highly pH-dependent, with peak adsorption at pH < 5 and limited adsorption above a pH of 8. Increases in soil water pH or dissolution of oxide phases can mobilize Mo.
- While the environmental chemistry of Mo has been well described in the literature, attempts to model its environmental fate and transport have been more limited. Surface complexation

models are promising and have been used to successfully model Mo adsorption using a relatively limited number of parameters.

- Overall, ash samples typically contain approximately 10-20 mg/kg Mo, but can have concentrations as high as 100 mg/kg or more. FGD SS typically contain 1-10 mg/kg Mo, and FGD gypsum samples typically contain < 1 mg/kg Mo. There is little information on the speciation of Mo in CCPs.
- Overall, Mo is typically present in CCP leachate of all types at concentrations of about 0.25 up to a few mg/L. These values exceed the US EPA's DWEL of 0.18 mg/L.
- The highest Mo leachate concentrations at CCP disposal sites are generally associated with fly ash disposed of in landfills (mean and median of 6.85 and 4.48 mg/L, respectively). The lowest leachate concentrations are associated with FGD gypsum (mean and median of 0.006 and 0.003 mg/L, respectively).
- The relatively high rate of leaching of Mo from fly ash, compared to the leaching rates of other trace metals such as arsenic and selenium, has been attributed to its association with soluble calcium salts. Over time, Mo leaching decreases as these salts become depleted from weathered CCPs.
- There is little information on the speciation of Mo in CCP leachate.

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A

SPECIFIC MOLYBDENUM SORBENTS

Iron/Manganese Oxides and Oxyhydroxides

Molybdate adsorption on iron oxides and oxyhydroxides (hematite, ferrihydrate, goethite, and amorphous iron oxides) has been shown to occur at a maximum at pH 4-5. Molybdate adsorption decreases rapidly above pH 5, with little to no molybdate adsorption occurring above pH 8 (Goldberg *et al*., 1996; Gustafsson, 2003). Molybdate adsorption by iron oxides has been modeled successfully using surface complexation models (SCMs) as inner-sphere complexation, forming strong coordinative bonds (Goldberg *et al*., 1996; Gustafsson, 2003; Xu *et al*., 2006). X-ray absorption spectroscopy (XAS) of Mo on goethite found that Mo surface complexation varies from tetrahedral to octahedral with decreasing pH, suggesting that Mo polymers may play an important role in the Mo adsorption mechanism at low pH (Arai, 2010). A Raman and Fourier transform infrared (FTIR) spectroscopic investigation of Mo on amorphous iron oxides found that Mo forms predominantly inner-sphere surface complexes at low pH and predominantly outer-sphere surface complexes at high pH (Goldberg *et al.*, 2008).

Mo is also adsorbed on manganese oxides. This relationship is especially apparent in marine systems where Mo is enriched in manganese oxide crusts, nodules, and sediments at a Mo:Mn molar ratio of 1.1×10^{-3} (Bertine and Turekian, 1973). The mechanism of Mo incorporation into manganese oxides is unknown.

Tetrathiomolybdate adsorption on goethite was investigated by Xu *et al*. (2006). Goethite showed a stronger affinity for tetrathiomolybdate than molybdate. At all pH levels, tetrathiomolybdate adsorption exceeded molybdate adsorption. Tetrathiomolybdate adsorption exhibited the same pH dependence seen for molybdate, with 100% adsorbed below pH 6 and a rapid decrease in adsorption until pH 8. Tetrathiomolybdate adsorption on goethite is more resistant to competition from phosphate (Xu *et al*., 2006). The resistance of goethite to tetrathiomolybdate desorption implies that tetrathiomolybdate may play an important role in the permanent fixation of Mo in soils and sediments.

Aluminum Oxides and Clay Minerals

Amorphous aluminum oxides, gibbsite, and aluminum-containing clay minerals have smaller adsorption capacity than iron and manganese oxides but can still represent a significant reservoir for Mo adsorption. Mo adsorption capacities in some soils have been shown to correlate with extractable aluminum (Barrow, 1977, as cited in Chappell and Peterson, 1977; Goldberg, 2010). These minerals adsorb molybdate very similarly to iron oxides, showing high adsorption at pH 4 followed by a rapid decrease in adsorption capacity (Goldberg *et al*., 1998). Molybdate adsorption on montmorillonite was best described using an outer-sphere, electrostatic attraction bond (Goldberg *et al*., 2008). Mo adsorption on aluminum oxides, kaolinite, and illite have all been best described as forming monodentate surface complexes with an inner-sphere adsorption mechanism (Goldberg *et al*., 2008). Again, complexation appears to be pH-dependent; the predominantly inner-sphere Mo-gibbsite surface complexes at low pH change to predominantly outer-sphere surface complexes at high pH. On gibbsite, this transition in complexation type occurs even more rapidly with increasing pH than on goethite, implying the Mo adsorbed onto aluminum oxides may be more easily desorbed than iron oxides (Goldberg *et al*., 2008).

Pyrite

Molybdate adsorption on pyrite has been investigated by Xu *et al*. (2006) and Bostick *et al*. (2003). Molybdate adsorbs strongly to pyrite under acidic pH, but it is readily desorbed with increased pH. X-ray absorption spectroscopy examination determined that molybdate forms bidentate, mononuclear complexes on FeS_2. Tetrathiomolybdate, on the other hand, appears to form highly stable Mo-Fe-S cubate-type clusters that resist desorption (Bostick *et al*., 2003). This supports the hypothesis that tetrathiomolybdate is the reactive Mo species in anoxic regions and ultimately may control Mo availability.

Organic Matter

Mo is not bound by most organic functional groups, but it is chelated by catechol groups (Wichard *et al*., 2009). Mo has been found to be bound and fixed by humic and fulvic acids (Smith *et al*., 1997). This adsorption appears to have an even greater pH dependence than iron oxides, with peak adsorption occurring at pH 3.5 on humic acid (Bibak and Borggard, 1994).

X-ray absorption spectra of Mo in black shales, anoxic sediments, and humic acid scavenging experiments have identified an organic form of Mo containing M-O double bonds and Mo-S-Fe bonds (Helz *et al*., 1996). Humic acid scavenging experiments (Helz *et al*., 1996) showed that, in oxic conditions, little Mo scavenging occurred above pH 5, but, in the presence of sulfide, humic acid was an effective scavenger at all pHs tested (5, 7, and 9). Helz *et al*. (1996) suggested that this was either the result of sulfidization of the humic acid or because the Mo-S-Fe bond is formed from humic bound iron. In oxic conditions, another X-ray absorption study (Wichard *et al*., 2009) found that Mo in the leaf litter of a temperate forest was bound by catechol-rich tannins; the authors found that molybdate will bind to leaf litter extract (LLE). This binding is pH-dependent, with the highest binding occurring at pH 6.1. It decreases slightly with decreased pH, but most Mo is still bound to the LLE at pH 4.7. At pH 9, only half the Mo is bound to the LLE. Binding to insoluble tannins may inhibit Mo leaching from surface soil and provide a source of bioaccessible Mo.

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